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ON THE ACTION OF AROMATIC SULPHONCHLORIDES ON UREA.

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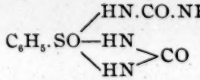
Some time ago Elander[1] found that benzenesulphonchloride acts on urea with elimination of hydrochloric acid to form a product which he represented by the formula

$$C_6H_5.SO.N_4H_5C_2O_2 + H_2O.$$

The action is between one molecule of the sulphonchloride and two of urea, and hydrochloric acid and, apparently, water are eliminated. Elander did not attempt to determine the constitution of the compound but at the time contented himself with making two suggestions. According to one, the compound is formed as a result of the two following reactions:

1. $C_6H_5.SO_2Cl + H_2N—CO—NH_2 = C_6H_5.SO_2HN.CO.NH_2 + HCl;$

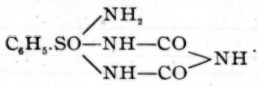
2. $C_6H_5.SO_2HN.CO.NH_2 + H_2N—CO—NH_2 =$



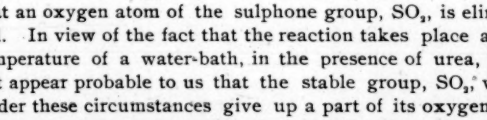
$+ H_2O.$

[1] Bull. Soc. Chim., 34, 207.

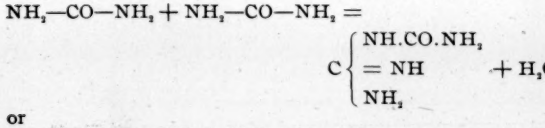
According to the other suggestion the product is a derivative of biuret, which may be represented by the formula



Both of these suggestions are based upon the assumption that an oxygen atom of the sulphone group, SO_2, is eliminated. In view of the fact that the reaction takes place at the temperature of a water-bath, in the presence of urea, it did not appear probable to us that the stable group, SO_2, would under these circumstances give up a part of its oxygen, and these experiments were undertaken with the view of determining the course of the reaction, if possible. The work has been entirely successful and has led to a simple and satisfactory explanation of the reaction. The product is a derivative of guanylurea, which has the constitution represented by the formula



A substance of this constitution is related to urea and its formation from urea is not surprising, though hitherto it has not been obtained in this way. It seems highly probable that in our experiments the sulphonchloride acts, in the first instance, as a dehydrating agent, thus causing the union of two molecules of urea with elimination of water:



or

This eliminated water does not, however, escape as such but reacts with the sulphonchloride to form the sulphonic acid and hydrochloric acid. The hydrochloric acid escapes while the sulphonic acid remains in combination with the base forming a salt which should be represented by the formula

$$C_6H_5.SO_3H.C_7H_8N_4O.$$

This is the *benzenesulphonate of guanylurea*, as we have shown by comparing the substance with the salt made by bringing together benzenesulphonic acid and guanylurea made according to the older methods described in the literature. The experimental details are given in the following paragraphs. The reaction was extended to paratoluenesulphonchloride, orthotoluenesulphonchloride, and to α- and β-naphthalenesulphonchlorides, the results obtained being entirely analogous to those obtained with benzenesulphonchloride.

I. Benzenesulphonchloride and Urea.

1. *Preparation of Guanylurea Benzenesulphonate.*—Twenty-five grams of benzenesulphonchloride and 20 grams of pulverized urea are brought together in a thick-walled beaker and heated in a water-bath to 100°. The mixture soon melts, forming two distinct layers which are mixed by thorough stirring. For a few minutes there is no evidence of action. After a short time the mixture begins to thicken. This is the critical stage of the reaction and requires close attention. Once begun it proceeds rapidly, and the mass solidifies in a few minutes. The beaker should be kept well immersed in the water, and the mass rapidly and thoroughly stirred. Unless these precautions are taken, the reaction becomes violent and the heat evolved at once decomposes any urea that is left. The reaction in this case takes an entirely different course and little or none of the desired product is obtained. As soon as the mass has solidified, it may safely be left to itself. The bath is kept at the boiling temperature and the contents of the beaker occasionally stirred until hydrochloric acid is no longer evolved. After the completion of the reaction, which usually requires from three to four hours, the mass should have the form of a white, crystalline powder. The product thus ob-

tained is allowed to cool and is then dissolved in 200 cc. boiling water. On standing, the product is deposited from the solution in colorless, wart-like aggregates, which can easily be purified by recrystallization from water. By cautious concentration, the mother-liquor yields a second crop of crystals. The sulphonate, when pure, melts at 216° C. (uncorr.). The yield approximates the weight of sulphonchloride used, or 60 to 70 per cent of the theoretical quantity. Analyses gave the following results:

I. 0.2162 gram substance gave 0.2928 gram CO_2 and 0.0921 gram H_2O.

II. 0.2076 gram substance gave 0.2817 gram CO_2 and 0.0846 gram H_2O.

III. 0.1978 gram substance gave 0.1764 gram $BaSO_4$.

IV. 0.1923 gram substance gave 0.1706 gram $BaSO_4$.

V. 0.1858 gram substance gave 35.6 cc. N at 22° C. and 763.4 mm. pressure.

VI. 0.2035 gram substance gave 38.6 cc. N at 19°.3 C. and 757 mm. pressure.

	Calculated for $C_8H_{12}SN_4O_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	36.92	36.93	37.0	....	....	....	....
H	4.62	4.76	4.55	....	....	....	....
N	21.54	....	....	....	....	21.73	21.62
S	12.31	....	....	12.25	12.2	....	....

Guanylurea benzenesulphonate obtained in this way always crystallizes in hard, wart-like masses unless allowed to crystallize from very dilute solutions by spontaneous evaporation, when it may be obtained in colorless plates. The sulphonate can be heated in the air to 160° C. without undergoing change, but above this temperature it slowly decomposes. The yield of the sulphonate is about 70 per cent of the theoretical. Guanylurea benzenesulphonate is difficultly soluble in cold water and in alcohol, insoluble in ether and in benzene.

Haag[1] and Baumann[2] have prepared guanylurea and investigated it to some extent. Baumann made it by heating together urea and a salt of guanidine:

$$CO(NH_2)_2 + CH_5N_3 = C_2H_6N_4O + NH_3.$$

[1] Ann. Chem. (Liebig), **122**, 25.

[2] Ber. d. chem. Ges., **7**, 1766.

This has, hitherto, been the most satisfactory method of preparation, but the new method above described gives a much better yield and is simpler. The evidence that our product is a salt of guanylurea was furnished by making the base by Baumann's method and bringing this together with benzenesulphonic acid in solution in water. The salt thus obtained proved to be identical with the product of the action of benzenesulphonic acid on urea. Further, the base was separated from the latter compound, and starting with this, other salts were made and these compared with those described by Haag. The two series were found to be identical.

For the purpose of separating the base from the sulphonate, advantage was taken of the fact established by Haag that, when a solution of a salt of guanylurea is heated with sodium hydroxide and copper sulphate, a characteristic rose-colored copper compound of the base is precipitated. This precipitate was easily formed from the sulphonate. It was filtered off, washed and suspended in water. Through this mixture hydrogen sulphide was passed until the compound was completely decomposed. A solution of the sulphide of the base was thus obtained, and this was used in the preparation of the salts. The salts prepared were the *acid carbonate*, $C_2H_6N_4O.H_2CO_3$, the *oxalate*, $C_2H_2O_4.2C_2H_6N_4O$, the *nitrate*, $C_2H_6N_4O.HNO_3$, the *chlorplatinate*, $(C_2H_6N_4O.HCl)_2PtCl_4$, and the *sulphate*, $(C_2H_6N_4O)_2H_2SO_4$. All of these have characteristic properties.

2. *Action of Hydrochloric Acid on Guanylurea Benzenesulphonate.*—Ten grams of the salt were heated in a sealed tube at 170° to 180° for six hours with hydrochloric acid prepared by mixing 1 part of the concentrated acid with 3 parts of water. Strong pressure was developed during the reaction in consequence of the evolution of carbon dioxide. The resulting product was dissolved in a small quantity of hot water, and, on cooling, a substance crystallized out that proved to be guanidine benzenesulphonate. It appeared in delicate leaflets or large colorless blades, according to the concentration and the rate of cooling of the solution. It was purified by recrystallization from water, and was then found to melt at 206°. It was compared with the salt made by bringing together

guanidine carbonate and benzenesulphonic acid, and the two substances were found to be identical. It is easily soluble in hot water, and somewhat difficultly in cold water. The reaction with hydrochloric acid takes place as represented in the following equation:

$$C_6H_5.SO_3H.H_2N.C.NH_2 + H_2O + HCl = \begin{matrix} \\ \| \\ N.CONH_2 \end{matrix}$$

$$C_6H_5.SO_3H.H_2N.C.NH_2 + CO_2 + NH_4Cl.$$
$$\|$$
$$NH$$

Analyses of the salt gave the following results: I, II, and VII were obtained with the product made from the salt of guanylurea, while III, IV, V, and VI were obtained with the product made from guanidine.

I. 0.2096 gram substance gave 35.3 cc. N at 20° C. and 767 mm. pressure.

II. 0.2036 gram substance gave 35.9 cc. N at 27° and 754 mm. pressure.

III. 0.21 gram substance gave 35.4 cc. N at 19° C. and 760 mm. pressure.

IV. 0.2118 gram substance gave 37.2 cc. N at 26° C. and 756 mm. pressure.

V. 0.1722 gram substance gave 0.1853 gram $BaSO_4$.

VI. 0.1801 gram substance gave 0.1961 gram $BaSO_4$.

VII. 0.2055 gram substance gave 0.2204 gram $BaSO_4$.

	Calculated for $C_6H_5SO_3H.CN_3H_5$.	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
N	19.35	19.42	19.31	19.38	19.39	....	....	....
S	14.75	....	....	....	....	14.78	14.96	14.73

3. *Action of Nitric Acid.*—To 10 grams of the pulverized material, fuming nitric acid is cautiously added. The reaction is vigorous and the material goes into solution with rapid evolution of fumes. The heat of reaction is sufficient to produce boiling of the solution. To secure a clean reaction a large excess of nitric acid is necessary and the solution is gently heated until there is no further evidence of action. The solution thus obtained is evaporated on the water-bath till the excess of nitric acid is expelled. The residue forms a

thick, gummy mass having a deep-yellow color. This is dissolved in a small quantity of boiling water and, upon cooling, nitroguanidine crystallizes out in an asbestos-like mass of fine needles. The nitroguanidine thus obtained is almost pure and can easily be obtained in pure condition by recrystallizing from water. It melts at 230° C. Ten grams of material treated with 20 cc. of fuming nitric acid gave 2.35 grams of nitroguanidine, which is nearly 60 per cent of the theoretical yield. The product thus obtained was shown by analysis, as well as by the preparation of a number of its derivatives described by Thiele,[1] to be identical with that described in the literature.

Analyses gave the following results:

I. 0.1367 gram substance gave 63.1 cc. N at 15° and 756 mm. pressure.

II. 0.1456 gram substance gave 66 cc. N at 11° C. and 756 mm. pressure.

	Calculated for $CN_4H_4O_2$.	Found. I.	II.
N	53.84	53.78	53.76

With phenol and sulphuric acid a green color was obtained which was changed to a yellowish-green by addition of an alkali.

The *silver salt* was obtained by dissolving the nitroguanidine in a cold solution of alkali and adding an ammoniacal solution of silver nitrate.

Nitroguanidine nitrate was made by dissolving the nitroguanidine in hot concentrated acid. On cooling, it crystallized in blades which melted at 140° C.

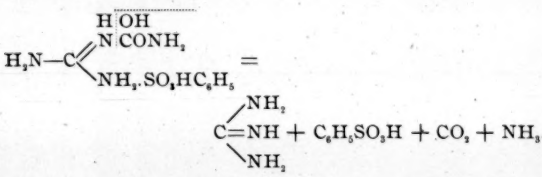
Amidoguanidine was obtained by bringing together 5 grams of the nitroguanidine in question, 20 grams of zinc dust, and sufficient ice and water to form a thick paste. To this mixture was added, gradually, 3 grams of diluted glacial acetic acid. When the reduction was complete the filtered solution was evaporated with sufficient nitric acid to expel the acetic acid. From the concentrated solution amidoguanidine nitrate crystallized out, melting at 144° C. By addition of copper acetate to a solution of this salt the characteristic blue *copper*

[1] Ann. Chem. (Liebig), **273**, 140 (1893).

compound was obtained. From a second solution of the salt, upon addition of ammonium picrate, the *picrate* was deposited in well-characterized yellow needles.

According to Limpricht[1] a mixture of the three isomeric mononitrobenzenesulphonic acids results from the nitration of benzenesulphonic acid. By neutralization of the mother-liquor from the nitroguanidine with potassium carbonate a mixture of the three potassium salts is apparently obtained. These salts are difficultly soluble and were obtained in well-crystallized form. No attempt was made to separate them.

The action of nitric acid on the sulphonate is partly represented by the equation:



The guanidine and benzenesulphonic acid thus formed are at once further acted upon by the nitric acid, and nitroguanidine and the nitrobenzenesulphonic acids are formed.

4. *Action of Barium Hydroxide.*—The material is boiled with an excess of barium hydroxide in a flask connected with a return condenser, the upper end of which is fitted with a tube containing soda-lime. The hydrolysis is complete after four to five hours' boiling. The separation of barium carbonate begins at once and ammonia is freely evolved during the operation. The excess of barium is precipitated with carbon dioxide and the filtered solution evaporated to a small volume. Barium benzenesulphonate crystallizes out from the solution in long, colorless prisms.

Analysis gave the following:

I. 0.2146 gram substance gave 0.1061 gram $BaSO_4$.
II. 0.2681 gram substance gave 0.1327 gram $BaSO_4$.
III. 0.343 gram substance lost 0.131 gram H_2O.

[1] Ann. Chem. (Liebig), 177, 60.

	Calculated for $(C_6H_5SO_2)_2Ba + H_2O$.	Found. I.	II.	III.
Ba	29.21	29.07	29.1	....
H_2O	3.84	....	....	3.82

To further characterize the product, the barium salt was converted into the potassium salt from which the chloride and the amide were made. The amide thus obtained melted at 152° C. The action of barium hydroxide is in accordance with what we should expect if the product under investigation is a derivative of guanidine. According to Baumann,[1] guanidine is unstable toward barium hydroxide, breaking down into ammonia and urea. Baumann has also shown that other salts of guanylurea conduct themselves in the same way toward barium hydroxide. Ten grams of the material were also boiled with a standard solution of barium hydroxide containing just enough barium to hydrolyze the product, *i. e.*, to combine with the carbon dioxide formed by the elimination of the urea residue. Again, only barium benzenesulphonate was obtained, the guanidine residue being destroyed.

5. *Action of Potassium Carbonate.*—The material is boiled with an excess of potassium carbonate for four to five hours. Ammonia and carbon dioxide are evolved during the reaction. The resulting solution is evaporated to a small volume and, upon cooling, guanidine benzenesulphonate crystallizes out. The product was found to be identical with that obtained by hydrolyzing the sulphonate with hydrochloric acid. This experiment was carried out to determine whether guanidine carbonate is formed under the conditions described, but only the sulphonate was obtained, this being less soluble than the carbonate.

II. Paratoluenesulphonchloride and Urea.

1. *Preparation of Guanylurea p-Toluenesulphonate.*—The method of preparation is quite similar to that used in the preparation of the benzenesulphonate; 25 grams of *p*-toluenesulphonchloride and 18 grams of urea are ground together and brought into a thick-walled beaker of about 250 cc. capacity. The mixture is heated in the water-bath to 100°. The mass soon melts and separates into two distinct layers which are

[1] Ber. d. chem. Ges., 6, 1376.

mixed by stirring. After a few minutes the mass begins to react. Once begun, the reaction proceeds very rapidly and requires careful attention at this point. To secure a clean reaction the beaker should be kept well immersed in the bath and the contents vigorously stirred, best with a spatula. If left alone the reaction becomes violent and a hard, amorphous mass is obtained which is difficultly soluble in water and cannot be recrystallized. As soon as the mass has solidified it may safely be left to itself. The bath is kept at the boiling temperature and the contents of the beaker occasionally stirred till hydrochloric acid is no longer evolved. After the completion of the reaction, which usually requires from three to four hours, the mass should have the form of a white crystalline powder. The product thus obtained is allowed to cool and is then dissolved in 150 cc. boiling water. On standing, the sulphonate is deposited from the solution in colorless, wart-like aggregates, which can easily be purified by recrystallization from water. It cannot be distinguished in appearance from the benzenesulphonate. The guanylurea *p*-toluenesulphonate melts at 224° (uncorr.). The yield is approximately the same as that of the benzenesulphonate—60 to 70 per cent.

The analyses gave the following results:

I. 0.2151 gram substance gave 0.3114 gram CO_2 and 0.0988 gram H_2O.

II. 0.2178 gram substance gave 0.3158 gram CO_2 and 0.103 gram H_2O.

III. 0.1668 gram substance gave 0.144 gram $BaSO_4$.

IV. 0.159 gram substance gave 0.1365 gram $BaSO_4$.

V. 0.2063 gram substance gave 35.8 cc. N at 13° and 757 mm. pressure.

VI. 0.2003 gram substance gave 36.1 cc. N at 20° and 755 mm. pressure.

	Calculated for $C_9H_{14}SN_4O_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	39.42	39.48	39.54	....	....	....	....
H	5.11	5.13	5.29	....	....	....	....
S	11.68	....	....	11.86	11.76	....	....
N	20.44	....	....	....	....	20.42	20.52

Prepared by the method just described, the sulphonate crystallizes in warts, unless allowed to separate from a very dilute solution by spontaneous evaporation. Under these conditions it may be obtained in colorless plates. It can be heated to 150° in the air without change, but above this temperature it slowly decomposes. The salt was also prepared by bringing together guanylurea and *p*-toluenesulphonic acid. It crystallized in plates, which had the same melting-point as the wart form, 224°.

2. *Action of Hydrochloric Acid.*—Ten grams of the product are heated in a sealed tube to 170° to 180° for six hours with about 20 cc. of hydrochloric acid (1 part of concentrated hydrochloric acid to 3 parts of water). Strong pressure is developed during the action and carbon dioxide escapes when the tube is opened. The resulting product is dissolved in a small quantity of hot water and the solution allowed to cool. Guanidine *p*-toluenesulphonate crystallizes out in delicate leaflets or large, colorless plates, depending on the concentration of the solution. The salt is purified by recrystallization from water and then has the melting-point 206°. The sulphonate was also made by bringing together guanidine carbonate and *p*-toluenesulphonic acid. The product thus obtained was compared with the sulphonate made as described above and the two were found to be identical. The salt is easily soluble in hot, tolerably difficultly soluble in cold, water. The reaction with hydrochloric acid may be represented by the following equation:

$$C_6H_4\begin{cases}CH_3(p)\\ SO_3H.H_2NC.NH_2\\ \quad\quad\|\\ \quad\quad N\,CONH_2\\ \quad\quad H\,OH\end{cases} = C_6H_4\begin{cases}CH_3(p)\\ SO_3H.CN_3H_5\end{cases} + CO_2 + NH_3.$$

Analyses gave the following results: III, IV, and VII were obtained from the product of hydrolysis, and I, II, V, and VI from the synthetically prepared product.

I. 1758 gram substance gave 27.6 cc. N at 20° C. and 767 mm. pressure.

II. 0.1873 gram substance gave 30.2 cc. N at 24° and 763.4 mm. pressure.

III. 0.1929 gram substance gave 30.8 cc. N at 24° and 774 mm. pressure.

IV. 0.1615 gram substance gave 26.5 cc. N at 27° and 764 mm. pressure.

V. 0.1649 gram substance gave 0.165 gram $BaSO_4$.

VI. 0.1671 gram substance gave 0.1695 gram $BaSO_4$.

VII. 0.1743 gram substance gave 0.1772 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{CH_3}_{SO_3.OH.CN_3H_5}$	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
N	18.18		18.14	18.16	18.25	18.19	....	....	....
S	13.85		....	....	....	....	13.75	13.93	13.96

3. *Action of Nitric Acid.*—To 10 grams of the product, 20 cc. of fuming nitric acid (sp. gr. 1.5) are cautiously added in small portions. The reaction is quite violent and the material passes into solution with copious evolution of dense fumes. The heat of reaction is sufficient to produce boiling. The solution is kept at the boiling-point by gently heating until there is no further evidence of action. The solution is then evaporated on the water-bath till the excess of nitric acid is expelled. The residue thus obtained forms a viscous mass having a deep-yellow color, and, on cooling, solidifies. This mass is dissolved in a small volume of hot water and, upon cooling, nitroguanidine separates out in the characteristic asbestos-like mass of fine needles. The product thus obtained is identical with that obtained from guanylurea benzenesulphonate.

Under the conditions of the reaction, the formation of one or more mononitrosulphonic acids is to be expected. By neutralizing the mother-liquor from the nitroguanidine with barium hydroxide a difficultly soluble salt is obtained. It crystallized in small plates of a pearly luster.

Analyses gave the following results:

I. 0.2942 gram anhydrous salt gave 0.1202 gram $BaSO_4$.

II. 0.2549 gram anhydrous salt gave 0.1047 gram $BaSO_4$.

III. 0.313 gram salt lost 0.0188 gram H_2O at 12°.

IV. 0.2712 gram salt lost 0.0163 gram H_2O at 12°.

	Calculated for $\left(C_6H_3(NO_2)\begin{cases}CH_3\\SO_3\end{cases}\right)_2Ba + 2H_2O$.	Found. I.	II.	III.	IV.
Ba	22.64	22.58	22.7	....	....
H_2O	5.95	....	....	6.0	6.01

This salt is probably derived from the acid of the formula $C_6H_3\begin{cases}CH_3\\NO_2(m)\\SO_2H(p)\end{cases}$. It has been described by Beilstein and Kuhlberg.[1]

4. *Urea and Paratoluenesulphonchloride in Alcoholic Solution.*—Twenty-five grams of *p*-toluenesulphonchloride are dissolved in the smallest possible quantity of alcohol, and to this solution is added a solution of 12 grams of urea in alcohol. The mixture is allowed to stand for several hours and then evaporated to a small volume. The product thus obtained is recrystallized from water. From a dilute aqueous solution it can be obtained in beautiful interlocked plates several centimeters in length. When pure it melts at 178° C.

Analyses gave the following results:

I. 0.2024 gram substance gave 0.3085 gram CO_2 and 0.0984 gram H_2O.

II. 0.2124 gram substance gave 0.3253 gram CO_2 and 0.1025 gram H_2O.

III. 0.2428 gram substance gave 0.3711 gram CO_2 and 0.117 gram H_2O.

IV. 0.1976 gram substance gave 20.4 cc. N at 19°.5 and 758 mm. pressure.

V. 0.2017 gram substance gave 20.63 cc. N at 18° and 764 mm. pressure.

VI. 0.203 gram substance gave 0.2096 gram $BaSO_4$.

	Calculated for $C_8H_{12}SN_2O_4$.	Found. I.	II.	III.	IV.	V.	VI.
C	41.61	41.59	41.8	41.71	....	....	....
H	5.21	5.33	5.39	5.39	....	....	....
N	12.14	....	....	....	12.16	12.14	....
S	13.87	....	....	....	....	....	14.14

[1] Ann. Chem. (Liebig), **155**, 18.

As is shown by the above analyses, the product contains the elements of one molecule of water more than is required by the formula for the simple ureid. As this water cannot be expelled by heat it seemed probable that the sulphonchloride had been hydrolyzed and that the product really obtained is the sulphonate of urea. This view was confirmed by bringing together urea and free *p*-toluenesulphonic acid. The resulting product was found to be identical with that obtained from the chloride. The formation of the sulphonate is to be explained by the fact that the sulphonchloride reacts with the alcohol, giving the free sulphonic acid which at once combines with the urea. It is interesting to note that urea *p*-toluenesulphonate is quite difficultly soluble in water.

III. Orthotoluenesulphonchloride and Urea.

1. *Preparation of Guanylurea o-Toluenesulphonate.*—Twenty-five grams of the chloride and 18 grams of urea are brought together in a thick-walled beaker of suitable capacity and heated to 100° on the water-bath. The mass soon melts, forming two distinct layers which, upon stirring, soon begin to react. Constant and thorough stirring greatly facilitate the reaction, which usually requires six to eight hours' heating for completion. A marked difference in the ease with which the isomeric toluenesulphonchlorides react with urea is thus shown, the parachloride reacting much more readily than the ortho. When the mass has completely solidified and no more hydrochloric acid is evolved, it is allowed to cool and is then dissolved in a small quantity of hot water. The sulphonate crystallizes in the characteristic form of warts. It cannot be distinguished in appearance from the *p*-toluenesulphonate with which it is isomeric. It melts at 205° (uncorr.). Treated with sodium hydroxide and copper sulphate, the characteristic rose-red copper derivative of guanylurea is obtained. The results of the analyses follow:

I. 0.2378 gram substance gave 42.2 cc. N at 21°.5 and 765.5 mm. pressure.

II. 0.2352 gram substance gave 42.8 cc. N at 24° and 762 mm. pressure.

III. 0.1727 gram substance gave 0.1497 gram $BaSO_4$.

IV. 0.1856 gram substance gave 0.1578 gram $BaSO_4$.

	Calculated for $C_9H_4SN_4O_4$.	Found. I.	II.	III.	IV.
N	20.44	20.3	20.46	....	....
S	11.68	....	....	11.89	11.68

Guanylurea *o*-toluenesulphonate was also made by bringing together *o*-toluenesulphonic acid and guanylurea. Thus formed it crystallizes in colorless plates, melting at 205°.

2. *Action of Nitric Acid.*—To 10 grams of the sulphonate 20 cc. of fuming nitric acid (sp. gr. 1.50) are cautiously added. The reaction is quite violent and the material at once passes into solution with copious evolution of dense fumes. The heat of reaction is sufficient to set up boiling. The solution is maintained at the boiling-point by gently heating until there is no further evidence of action. The solution is then evaporated on the water-bath till the excess of nitric acid is expelled. The residue thus obtained forms a viscous mass of a deep-yellow color and solidifies upon cooling. The product is dissolved in a small quantity of boiling water and, upon cooling, nitroguanidine crystallizes out in the characteristic asbestos-like mass of fine needles. The mother-liquor was not examined for the nitrotoluenesulphonic acids.

IV. α-Naphthalenesulphonchloride and Urea.

1. *Preparation of Guanylurea α-Naphthalenesulphonate.*—Twenty grams of α-naphthalenesulphonchloride and 12 grams of urea are heated on the water-bath to 100°. The mixture soon melts, forming two distinct layers which are mixed by stirring. The resulting oil gradually thickens and finally solidifies. To insure a clean reaction the mixture must be thoroughly and constantly stirred. As soon as the mass has solidified it may safely be left to itself. The bath is kept at the boiling temperature until hydrochloric acid is no longer evolved. After cooling, the product is dissolved in boiling water. The sulphonate is deposited in the characteristic wart-like masses. It is markedly less soluble, both in cold and in hot water, than the sulphonates already described. With sodium hydroxide and copper sulphate it yields the characteristic copper derivative of guanylurea. The sulphonate melts at 223° C.

Analyses gave the following results:

I. 0.2422 gram substance gave 38.0 cc. N at 22° and 768.3 mm. pressure.

II. 0.2035 gram substance gave 32.05 cc. N at 21°.5 and 761 mm. pressure.

III. 0.379 gram substance gave 0.285 gram $BaSO_4$.

IV. 0.2348 gram substance gave 0.1796 gram $BaSO_4$.

	Calculated for $C_{12}H_{14}SN_4O_4$.	Found. I.	II.	III.	IV.
N	18.06	17.98	17.95	....	....
S	10.32	....	....	10.33	10.5

The sulphonate was also prepared by bringing together the sulphonic acid and guanylurea. This synthesis is notable as being the only one in which the sulphonate was obtained in the wart-like form.

2. *Action of Hydrochloric Acid.*—Ten grams of the product are heated in a sealed tube for six hours at 150° with about 20 cc. of hydrochloric acid (1 part concentrated hydrochloric acid and 3 parts water). A higher temperature is to be avoided during the reaction since α-naphthalenesulphonic acid is unstable above 150°. The resulting product is crystallized from water. It is guanidine α-naphthalenesulphonate as was shown by preparing the salt from guanidine carbonate and the free sulphonic acid. From a dilute aqueous solution it crystallizes in large rosettes of colorless needles which are difficultly soluble in cold water. The salt has no definite melting-point, a fact which is probably due to the instability of α-naphthalenesulphonic acid at high temperatures.

V. β-Naphthalenesulphonchloride and Urea.

1. *Preparation of Guanylurea β-Naphthalenesulphonate.*—Twenty grams of β-naphthalenesulphonchloride and 12 grams of urea are heated together in a thick-walled beaker to 100° on the water-bath. The mass begins to melt at once and soon separates into two distinct layers, which are mixed by stirring. Once begun the reaction proceeds rapidly and requires close attention at this stage. The beaker should be kept well immersed in the water and the contents thoroughly stirred to secure a clean reaction. Unless these pre-

cautions are taken the reaction becomes violent and takes an entirely different course. Here, again, there is to be noted a marked difference in the ease with which α- and β-naphthalenesulphonchlorides react with urea. The β-sulphonchloride reacts much more readily than the α-sulphonchloride. The bath is kept at the boiling temperature and the contents of the beaker occasionally stirred until no more hydrochloric acid is evolved. After the completion of the reaction, which usually requires from three to four hours, the mass is allowed to cool and is then dissolved in hot water. The sulphonate is deposited in hard masses, consisting of very fine blades. It is purified by recrystallizing from water. It is notable as being the only sulphonate thus far studied which does not crystallize in the wart form when prepared from the sulphonchloride and urea, and as being the most difficultly soluble in water. Guanylurea β-naphthalenesulphonate melts at 237° (uncorr.). Treated with sodium hydroxide and a dilute solution of copper sulphate it yields the copper derivative of guanylurea.

The analyses gave the following results:

I. 0.197 gram substance gave 30.7 cc. N at 21° and 768 mm. pressure.

II. 0.2061 gram substance gave 31.4 cc. N at 17° and 769 mm. pressure.

III. 0.1718 gram substance gave 0.1306 gram $BaSO_4$.

IV. 0.2093 gram substance gave 0.1593 gram $BaSO_4$.

	Calculated for $C_{13}H_{14}SN_4O_4$.	Found.			
		I.	II.	III.	IV.
N	18.06	17.94	17.9	....	....
S	10.32	....	....	10.44	10.46

The sulphonate was also made by bringing together the sulphonic acid and guanylurea, and this was found to be identical with that described above.

2. *Action of Hydrochloric Acid.*— Ten grams of the product are heated in a sealed tube at 160° for six hours with about 20 cc. of strong hydrochloric acid. Strong pressure is developed in the tube. The product obtained is guanidine α-naphthalenesulphonate. From a dilute solution it crystallizes in clusters of long colorless needles; from a concentrated solution in very fine needles or in fine blades. The sulphonate is difficultly

soluble in cold water. It melts at 259°. The salt was also prepared, for the purpose of comparison, by bringing together guanidine carbonate and β-naphthalenesulphonic acid. The two products were found to be identical.

The treatment of urea with an aromatic sulphonchloride is thus shown to furnish a convenient method for the preparation of guanylurea and also of guanidine, though the preparation of the latter by the method of Volhard[1] from ammonium sulphocyanate is probably somewhat more economical.

ON THE ACTION OF AROMATIC SULPHONCHLORIDES ON THIOUREA.

By Ira Remsen and H. J. Turner.

The interesting results obtained in studying the action of aromatic sulphonchlorides on urea, an account of which is given in the preceding article, led to the experiments described in this article. As will be seen, the action of the sulphonchlorides on thiourea is entirely different from that which takes place with urea itself. The reaction is somewhat complicated. In the first place the thiourea abstracts the chlorine from the sulphonchloride and forms with this chlorine the *dithiourea dichloride*, $(CSN_2H_4)_2Cl_2$, first obtained by Claus[2] by passing chlorine into a cold saturated aqueous or alcoholic solution of thiourea. The residues of the two molecules of the sulphonchloride then react with two more molecules of the thiourea. Reduction takes place with separation of sulphur and probably the formation of cyanamide. The reduction of the two residues of the sulphonchloride leads to the formation of a disulphoxide. For example, in the case of benzene sulphonchloride the reaction takes place as represented in the following equation:

$$\begin{matrix} C_6H_5.SO_2 \\ C_6H_5.SO_2 \end{matrix} + 2CSN_2H_4 = \begin{matrix} C_6H_5.SO \\ | \\ C_6H_5.SO \end{matrix} + 2CNNH_2 + 2S + 2H_2O.$$

The product represented by the formula $\begin{matrix} C_6H_5.SO \\ | \\ C_6H_5.SO \end{matrix}$, is the *ben-*

[1] J. prakt. Chem. [2], 9, 15.

[2] Ann. Chem. (Liebig), 179, 139 (1875).

zene disulphoxide or *phenyl benzenethiosulphonate* of Otto.[1] As will be pointed out further on, Otto holds that this substance has the structure represented by the formula $C_6H_5.SO_2.SC_6H_5$, —that it is in fact the phenyl ester of benzenethiosulphonic acid. He obtained it by means of quite different reactions but we have established the identity of his product with ours.

In brief, then the changes that take place when benzenesulphonchloride and this urea are brought together in alcoholic solution are represented by the following two equations:

(1) $2C_6H_5.SO_2Cl + 2CSN_2H_4 = (C_6H_5SO_2)_2 + (CSN_2H_4)_2Cl_2$;

(2) $(C_6H_5SO_2)_2 + 2CSN_2H_4 = (C_6H_5SO)_2 + 2CNNH_2 + 2S + 2H_2O$.

The reactions take place so smoothly that they furnish an excellent method for the preparation of the disulphoxide—apparently better than those made use of by Otto.

The action of paratoluenesulphonchloride on thiourea has also been studied and we have found that it takes place in general the same as that of benzenesulphonchloride on urea.

I. Benzenesulphonchloride and Thiourea.

When benzenesulphonchloride and urea in the dry condition are gently warmed together, reaction takes place when the temperature of 40° is reached. Heat is evolved, the mass suddenly turns yellow, sulphur separates, and hydrochloric acid is given off in quantity. The reactionis almost violent, and is complete in a few minutes. When cold, the mixture thus formed consists of a heavy, yellowish oil saturated with sulphur, crystals of sulphur, and a white, amorphous solid. Sometimes the reaction takes place slowly. This seems, however, to make no difference in the result.

The yellowish oil is soluble in carbon bisulphide, alcohol, acetic acid, and ether, but insoluble in water. It is not volatile with water wapor. It is saturated with sulphur which slowly crystallizes out. This oil could not be purified. When alcohol is used as a solvent the reaction takes place quietly with but little elevation of temperature. After the reaction is over fine needles separate, and the deposit is increased by the

[1] Ann. Chem. (Liebig), **145**, 317 (1868).

addition of ether. The crystals having been filtered off, water is added to the mother-liquor when a colorless oil is thrown down. This solidifies after a time. The needles first deposited proved to be dithiourea dichloride; the product that appears first as an oil, which then solidifies, proved to be benzene disulphoxide (or phenyl benzenethiosulphonate). The best method of procedure was found to be the following:

Thiourea (4.6 grams) was dissolved in 150 cc. alcohol with the aid of heat, and benzenesulphonchloride (5 grams) added to this solution after it had cooled to the temperature of the room. The mixture became slightly warm. On cooling, fine crystals separated, and the quantity of the deposit was increased by the addition of 150 cc. ether. After two hours the crystals were filtered off, washed, at first with a mixture of alcohol and ether, then with ether, and finally dried on paper, and over sulphuric acid in a desiccator. The product thus prepared was found to be quite pure. If allowed to crystallize slowly from the alcoholic solution some change takes place in it. It then contains sulphur, from which it is impossible to separate it.

The alcohol-ether solution filtered from the crystals was treated with four times its volume of water. This caused the precipitation of the oil, above referred to. The supernatant liquid was decanted, and the oil washed with water. After removal of the water the oil was allowed to stand in a desiccator over sulphuric acid, and in about twelve hours it solidified. It was then purified by three crystallizations from ether, when it was found to melt sharply at 45°. This product is benzene disulphoxide. That its formation is not due to the action of the water was shown by rapidly evaporating by means of a blast of air a portion of the alcohol-ether solution when a semi-liquid mass was obtained in which small crystals were embedded. These melted at 45° when recrystallized from ether. A second portion of the alcohol-ether solution was allowed to evaporate slowly over sulphuric acid in a partial vacuum and in this case also the disulphoxide was obtained in crystals which, when crystallized from ether, melted at 45°.

When, however, the alcohol-ether solution from which the dithiourea dichloride and the benzene disulphoxide had been

removed was evaporated on a water-bath, a dark, thick liquid containing sulphur and phenyl sulphydrate was obtained. The latter was detected by its odor and by the characteristic test. A small portion was heated in a test-tube in the open end of which was a strip of paper saturated with a solution of lead acetate, when the yellow coloration of lead mercaptide was obtained.

The yield of the dithiourea dichloride corresponds to about 90 per cent of the chlorine contained in the sulphonchloride. In one experiment 5 grams of the sulphonchloride gave 2.95 grams of the dichloride. In another 8.46 grams of the sulphonchloride gave 5.16 grams of the dichloride.

The yield of the disulphoxide corresponds to over 50 per cent of the phenyl contained in the sulphonchloride. This is 50 per cent better than by other methods hitherto employed. In one experiment 5 grams of the sulphonchloride gave 1.91 grams of the disulphoxide. In another 200 grams of the sulphonchloride gave 83 grams of the disulphoxide in the crystallized condition.

Dithiourea Dichloride.—This substance is soluble in water and alcohol, from which it can be crystallized only with difficulty, and when thus obtained, it always contains sulphur. From hydrochloric acid it can be easily obtained in transparent needles. It is insoluble in ether. It decomposes at 80° C. Alcohol and water decompose it slowly, alkalies rapidly, into hydrochloric acid, sulphourea, and cyanamide, with the separation of one-half its sulphur, as the following figures show:

1.9572 dithiocarbamide dichloride gave 0.2760 gram sulphur, or 14.12 per cent. The sulphur calculated for $(CSN_2H_4)_2Cl_2$ is 28.72 per cent., one-half of which is 14.36 per cent.

The analyses gave the following results:

I. 0.5761 gram substance gave 0.7336 gram AgCl (31.63 per cent Cl) and 1.1949 grams $BaSO_4$ (28.48 per cent S).

II. 0.1789 gram substance gave 0.2293 gram AgCl (31.84 per cent Cl) and 0.3727 gram $BaSO_4$ (28.61 per cent S).

III. 0.1885 gram substance gave 0.0739 gram CO_2 (10.69 per cent C) and 0.0606 gram H_2O (3.58 per cent H).

	Calculated for $(CSN_2H_4)_2Cl_2$.	Found. I.	II.
C	10.77	10.60	....
H	3.55	3.58	....
S	28.72	28.48	28.61
Cl	31.78	31.63	31.84

Claus[1] first prepared dithiourea dichloride by passing dry chlorine into a cold saturated aqueous or alcoholic solution of sulphourea :

$$2CSN_2H_4 + 2Cl = (CSN_2H_4)_2Cl_2.$$

McGowan[2] prepared it by the action of trichlormethylsulphonchloride on sulphourea :

$$4CSN_2H_4 + 2CCl_3SO_2Cl = (CSN_2H_4)_2Cl_2 + CSN_2H_3.CCl_3SO_2 + CSN_2H_4.CCl_3SO_2H.$$

Under similar conditions methylsulphon- and dichlormethylsulphonchlorides, CH_3SO_2Cl and $CCl_2H.SO_2Cl$, yield the same product, as does also phosphorus oxychloride.

Dibromsuccinic acid was converted by Nencki and Sieber[3] into fumaric acid by boiling with it sulphourea, under which conditions, not the dibromide, but its decomposition-products were obtained, thus :

$$\begin{matrix}COOH—CHBr\\ \quad\quad|\\ COOH—CHBr\end{matrix} + CSN_2H_4 = \begin{matrix}CH—COOH\\ \quad\quad\|\\ CH—COOH\end{matrix} + CNNH_2 + S + 2HBr.$$

While the sulphonchlorides add chlorine to sulphourea easily, the chlorine acting like free chlorine, the chlorides of carboxyl acids do not.

With benzoyl chloride and sulphourea, Pike[4] obtained benzoyl thiocarbamide,

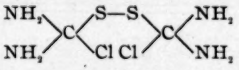
$$C_6H_5.COCl + CSN_2H_4 = C_6H_5CO.CSN_2H_3 + HCl.$$

With acetyl chloride Claus[5] obtained an addition-product, thus :

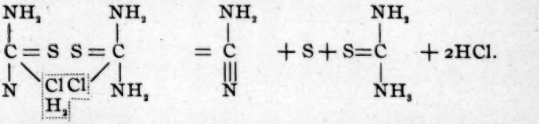
[1] Ann. Chem. (Liebig), **179**, 139 (1875).
[2] J. Chem. Soc., **49**, 191 (1896).
[3] J. prakt. Chem., **25**, 79 (1882).
[4] Ber. d. chem. Ges., **6**, 725 (1873).
[5] *Ibid.*, **8**, 41 (1875).

$$CSN_2H_4 + CH_3COCl = CSN_2H_4.CH_3COCl.$$

The percentage composition found by analysis agrees as well, of course, for a monosubstitution-product, CSN_2H_3Cl, as for a diaddition-product, $(CSN_2H_4)_2Cl_2$. The very curious decomposition of the substance by water into cyanamide, sulphourea, sulphur, and hydrochloric acid led Claus[1] to consider the substance a dichloride of dithiocarbamide, whose structure is represented thus:



and its decomposition by the equation:



From the ease with which the sulphur separates, the two sulphourea molecules are believed to be united through sulphur. The sulphur is doubly linked to carbon in sulphourea. By breaking this double bond, it becomes possible for the sulphur to unite with the sulphur of a second molecule, forming a dithiourea, which would be an unsaturated compound, capable of taking up two halogen atoms.

As will be shown farther on, the behavior of the dichloride towards potassium benzenesulphinate is strictly analogous to the action of dihalogen addition-products of certain unsaturated hydrocarbons, for example, stilbene dibromide,

$$C_6H_5CHCl = ClHC.C_6H_5,$$

toward the sulphinate. The dichloride behaves fully in accord with the formula of Claus.

This tendency of sulphourea to polymerize, to form an unsaturated dithiocarbamide, seems to explain why it acts differently from ordinary urea toward the sulphonchlorides. The molecule of sulphourea itself is not double; it corresponds to the single formula, as is shown by the following determination of its molecular weight by the freezing-point method:

[1] Ann. Chem. (Liebig), **179**, 139 (1875).

	I.	II.	III.
Weight of substance	2.3145	1.7584	3.4861
Weight of water	54.0029	46.0813	54.0029
Freezing-point lowering	1.029° C.	0.872°	1.295°

	Calculated.	Found. I.	II.	III.
Molecular weight	76	78.3	82.3	79.4

Benzene Disulphoxide.—Benzene disulphoxide, or phenyl ester of benzenethiosulphonic acid, is a colorless transparent solid, melting at 45° C.; very soluble in ether and benzene, less in alcohol, and insoluble in water. By evaporation of its ether solution it is obtained in large prisms, one of which was 2.5 cm. in length.

The analyses gave the following results:

I. 0.1407 gram substance gave 0.2960 gram CO_2 (57.38 per cent C), and 0.0496 gram H_2O (3.92 per cent H).

II. 0.2137 gram substance gave 0.4501 gram CO_2 (57.44 per cent C) and 0.0806 gram H_2O (4.19 per cent H).

III. 0.1997 gram substance gave 0.3759 gram $BaSO_4$ (26.24 per cent S).

IV. 0.1318 gram substance gave 0.2439 gram $BaSO_4$ (25.41 per cent S).

	Calculated for $C_{12}H_{10}S_2O_2$.	Found. I.	II.
C	57.6	57.38	57.44
H	4.0	3.92	4.19
S	25.6	26.24	25.41

The molecular weight of the disulphoxide was determined by the freezing-point method with benzene as the solvent. The results show that the molecular weight is correctly represented by the formula $C_{12}H_{10}S_2O_2$.

The figures follow:

	I.	II.
Weight of substance	2.8421	4.1104
Weight of benzene	47.7407	47.7407
Freezing-point lowering	1.145° C.	1.640°

	Calculated for $C_{12}H_{10}S_2O_2$.	Found. I.	II.
Molecular weight	250	254.7	257.2

The disulphoxide was saponified by potassium hydroxide

to potassium benzenesulphinate and phenyl disulphide according to the equation

$$3C_{12}H_{10}SO_4 + 4KOH = 4C_6H_5SO_2K + (C_6H_5)_2S_2 + 2H_2O.$$

Five grams substance were dissolved in 50 cc. alcohol, 3 grams potassium hydroxide added, and the whole boiled with return condenser on a water-bath for one hour. When cooled the reaction mixture consisted of a solid cake and a liquid. The solid was redissolved in hot alcohol from which it crystallized in thin needles, melting at 60° C. A small portion was reduced by zinc and hydrochloric acid, yielding the characteristic phenyl sulphydrate. The solid was phenyl disulphide, $(C_6H_5)_2S_2$. The liquid portion was evaporated to dryness, and the residue extracted with alcohol. This was evaporated, dissolved in a little water, and dilute sulphuric acid added, when, upon cooling, benzenesulphinic acid crystallized out which melted at 83° C. The identification of the benzene disulphoxide with that prepared by Otto was complete.

II. Paratoluenesulphonchloride and Sulphourea.

Ten grams of *p*-toluenesulphonchloride were dissolved in 300 cc. alcohol and added to 8 grams sulphourea dissolved in alcohol; this was in the proportion of 1 molecule of chloride to 2 of sulphourea. 500 cc. ether were added to cause the separation of the dithiourea dichloride, which was filtered off, washed, and dried. The *p*-toluene disulphoxide was then precipitated by adding three volumes of water, separated by decantation, washed, and allowed to stand over night, when it solidified. When recrystallized twice from ether, *p*-toluene disulphoxide melted at 78° C.

Paratoluene Disulphoxide.—This, like benzene disulphoxide, is soluble in ether, benzene, and alcohol, insoluble in water. When first precipitated it forms a colorless oil, solidifying slowly. It crystallizes in prisms, melting-point 78° C.

Analyses gave the following results:

I. 0.2304 gram substance gave 0.5096 gram CO_2 (60.32 per cent C) and 0.1062 gram H_2O (5.04 per cent H).

II. 0.1922 gram substance gave 0.3248 gram $BaSO_4$ (23.20 per cent S).

III. 0.2376 gram substance gave 0.3957 gram $BaSO_4$ (22.87 per cent S).

	Calculated for $C_{14}H_{14}S_2O_2$.	Found. I.	II.
C	60.43	60.32	....
H	5.04	4.12	....
S	23.02	23.20	22.87

The molecular weight was determined by the freezing-point method and it was found to be that corresponding to the formula $C_{14}H_{14}S_2O_2$. The figures obtained follow:

	I.	II.
Weight of benzene	43.5906	43.5906
Weight of substance	2.4622	3.9117
Freezing-point lowering	1.021°	1.541°

	Calculated for $C_{14}H_{14}S_2O_2$.	Found. I.	II.
Molecular weight	278	282.6	285.3

The disulphoxide was also saponified by potassium hydroxide, yielding tolyl disulphide, $(C_7H_7)_2S_2$, which melted at 41°, and potassium *p*-toluenesulphinate, from which was obtained the sulphinic acid melting at 80°. The reaction takes place according to the equation

$$3C_{14}H_{14}S_2O_2 + 4KOH = 4C_7H_7SO_2K + (C_7H_7)_2S_2 + 2H_2O.$$

No doubt remained that the substance was the *p*-toluenedisulphoxide of Otto.

III. Ammonium Sulphocyanate and Benzenesulphonchloride.

Ammonium sulphocyanate and benzenesulphonchloride were brought together in alcohol to ascertain if the sulphocyanate would act like its isomer, sulphourea.

Ten grams benzenesulphonchloride (1 molecule) were brought together with 8.5 grams ammonium sulphocyanate (2 molecules) in alcohol. Reaction was started on the water-bath, when a golden-yellow powder was precipitated. It was very slightly soluble in alcohol, insoluble in water, ether, and benzene. It did not melt at 230° C. Yield 8.3 grams. No disulphoxide, however, was precipitated upon addition of water to filtrate. On account of the complex nature of the sulphocyanic acid derivatives and the impossibility of obtain-

ing the above substance in crystalline form, it was not further studied.

IV. Dithiocarbamide Dichloride and Salts of Sulphinic Acids.

As sulphourea and benzenesulphonchloride give benzene disulphoxide, it appeared possible that potassium sulphinate and dithiourea dichloride might give the same compound. If the former react according to the equation

$$2C_6H_5SO_2Cl + 4CSN_2H_4 = (CSN_2H_4)_2Cl_2 + [(C_6H_5SO_2)_2(CSN_2H_4)_2],$$

the latter might react thus:

$$(CSN_2H_4)_2Cl_2 + 2C_6H_5SO_2K = 2KCl + [(C_6H_5SO_2)_2(CSN_2H_4)_2].$$

According to this equation the disulphoxide is formed from the intermediate compound $[(C_6H_5SO_2)_2(CSN_2H_4)_2]$, which may be called dithiourea dibenzenesulphinate. Whether this intermediate compound is formed or not, benzene disulphoxide is formed as a product of the action of dithiourea dichloride on potassium benzenesulphinate.

Ten grams of potassium benzenesulphinate were dissolved in absolute alcohol and added to a cold concentrated alcoholic solution of 6.3 grams of dithiocarbamide dichloride. The potassium chloride was filtered off, dried, and weighed; yield, 3.8 grams. Water was added to the filtrate to precipitate the disulphoxide. It came down as a colorless oil and was treated in the usual way as described above, when it was obtained well crystallized, melting at 45° C. The yield was 6.94 grams, containing 51.9 per cent of the total phenyl of the acid chloride. Upon evaporation, the mother-liquor yielded sulphur and a sulphydrate. When the substances were brought together in water instead of alcohol, the mixture at once turned white from the drops of oil held in suspension, which, upon settling to the bottom of the vessel, left the supernatant liquid clear. After twelve hours the oil, which had now solidified, was washed with water and treated with ether, in which it was not completely soluble. From the ether solution benzene-disulphoxide was obtained melting at 45° C. The residue insoluble in ether was soluble in hot alcohol, from which a sub-

stance crystallized in fine white crystals. This melted at 99°.5 and was found to be free of nitrogen. The quantity of the substance was too small to permit of an analysis. Upon platinum foil it burned, showing it to be organic.

The *p*-toluene disulphoxide was prepared in a similar way. Here, too, was obtained a small quantity of a white substance crystallizing from alcohol in needles, melting at 155° to 158° C. It was likewise free of nitrogen.

Märcker[1] was the first to prepare *p*-toluene disulphoxide. He made it by oxidizing benzyl sulphydrate with nitric acid, and he gave it the name oxybenzyl disulphide. The reaction is expressed by the equation

$$2C_7H_7.SH + 3O = C_{14}H_{14}S_2O_2 + H_2O.$$

Otto[2] was the next to prepare the substance, and he first prepared the homologous phenyl compound. He obtained the compounds by heating the corresponding sulphinic acids at 120° in closed tubes. Benzenesulphinic acid yields benzene disulphoxide and sulphonic acid,

$$3C_6H_5SO_2H = C_{12}H_{10}S_2O_2 + C_6H_5SO_3H + H_2O.$$

Otto and Pauly[3] obtained the disulphoxide from the sulphinates of the alkalies by the action of dehydrating agents, as sulphuric acid and phosphorus pentoxide. With potassium benzenesulphinate the reaction takes place as represented in the equation

$$3C_6H_5SO_2K + H_2SO_4 = C_{12}H_{10}S_2O_2 + C_6H_5SO_3K + K_2SO_4 + H_2O.$$

Otto[4] treated the compounds with zinc and thus obtained zinc mercaptide and zinc sulphinates, and for this reason he considered the so-called disulphoxides to be thioesters. Benzene disulphoxide is accordingly the phenyl ester of benzenethiosulphonic acid. The action of zinc is represented thus:

$$\begin{matrix} C_6H_5SO_2SC_6H_5 \\ C_6H_5SO_2SC_6H_5 \end{matrix} + 2Zn = \begin{matrix} C_6H_5SO_2 \\ C_6H_5SO_2 \end{matrix}\!\!>\!Zn + Zn\!<\!\begin{matrix} SC_6H_5 \\ SC_6H_5 \end{matrix}.$$

[1] Ann. Chem. (Liebig), **136**, 75 (1865).
[2] *Ibid.*, **145**, 10, 317 (1868).
[3] Ber. d. chem. Ges., **9**, 1640 (1876).
[4] *Ibid.*, **10**, 2181 (1877).

The disulphoxide differs from the thioester in the position of one oxygen atom, thus :

C_6H_5SO — C_6H_5SO — Disulphoxide.

$C_6H_5SO_2$ — C_6H_5S — Thioester.

The first contains tetravalent sulphur; the latter a hexavalent sulphur atom, united with oxygen, and a bivalent sulphur atom not united with oxygen. Otto did not, however, succeed in effecting the synthesis of the compound by methods applicable to the preparation of the aliphatic thioesters. In his latest article (1896) he uses the term disulphoxide with thioester in parenthesis.

Escales[1] found that the disulphoxide is formed when phenylhydrazine reacts with benzenesulphinic acid to form benzenesulphonphenylhydrazide, thus :

$$3C_6H_5SO_2H + C_6H_5HN.NH_2 = C_6H_5.HN.NH.SO_2C_6H_5 + C_{12}H_{10}S_2O_2 + H_2O.$$

The disulphoxide was also obtained by Otto[2] by the action of stilbene dibromide on sodium benzenesulphinate, when sodium bromide, stilbene (diphenylethylene) and a peculiar disulphone were formed :

$$\begin{matrix} C_6H_5.CHBr \\ | \\ C_6H_5.CHBr \end{matrix} + 2C_6H_5SO_2Na = 2NaBr + \begin{matrix} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{matrix} + \left[\begin{matrix} C_6H_5SO_2 \\ | \\ C_6H_5SO_2 \end{matrix}\right].$$

The latter is incapable of existence in the presence of water, with which it forms sulphinic and sulphonic acids,

$$\begin{matrix} C_6H_5SO_2 \\ | \\ C_6H_5SO_2 \end{matrix} + \begin{cases} HO \\ H \end{cases} = C_6H_5SO_2H + C_6H_5SO_3H,$$

so that it may be regarded as a double anhydride of sulphinic and sulphonic acids, which yields the anhydrides of these two acids.

[1] Ber. d. chem. Ges., **18**, 1893 (1883).
[2] J. prakt. Chem., **53**, 1 (1896).

$$2\begin{matrix}C_6H_5SO_2\\C_6H_5SO\end{matrix}\!\!>\!O = \begin{matrix}C_6H_5SO_2\\C_6H_5SO_2\end{matrix}\!\!>\!O + \begin{matrix}C_6H_5SO\\C_6H_5SO\end{matrix}\!\!>\!O.$$

Then the sulphinic acid changes, especially under pressure, into sulphonic acid and disulphoxide,

$$3C_6H_5SO_2H = C_6H_5SO_3H + C_{12}H_{10}S_2O_2.$$

In stilbene dibromide the two halogens are linked to different carbon atoms; if the two halogen atoms are linked to the same carbon atom, the disulphoxide is not obtained, but a sulphone.

Thus, with benzal chloride Otto[1] obtained chlorbenzylidene-phenylsulphone,

$$C_6H_5.CHCl + C_6H_5SO_2Na = C_6H_5CHCl.SO_2.C_6H_5 + NaCl.$$

The action of dithiourea dichloride with benzenesulphinate is similar to that of stilbene dibromide with the sulphinate. In both cases the disulphoxide is formed.

ON THE ACTION OF THE CHLORIDES OF ORTHOSULPHOBENZOIC AND OF PARANITROORTHOSULPHOBENZOIC ACIDS ON UREA.

By Willis B. Holmes.

It was thought that the two isomeric chlorides of orthosulphobenzoic acid and the corresponding chlorides of paranitroorthosulphobenzoic acid might react with urea in different ways. This was found not to be the case. The two isomeric chlorides both gave the same products, and these proved to be quite different in character from those obtained when a simple aromatic sulphonchloride is allowed to act upon urea (see the two preceding articles).

Chlorides of Orthosulphobenzoic Acid. — Some changes have been made in the method adopted in passing from benzoic sulphinide to these chlorides. A brief account of the improved method follows: Two hundred grams of the purest commercial sulphinide[2] (saccharin) are placed in a large evap-

[1] J. prakt. Chem., **148**, 517 (1889).

[2] I take pleasure in thanking the firm, Von Heyden, Radebeul, Germany, for sending me an abundant supply of the pure sulphinide.—I. R.

orating dish with 3 liters of water and 250 cc. of ordinary dilute hydrochloric acid. This mixture is then boiled for five or six hours, the volume being kept nearly constant until the sweet taste of the saccharin has entirely disappeared. It is then evaporated to about a liter, allowed to cool, filtered, and evaporated to dryness. The acid ammonium salt of orthosulphobenzoic acid thus obtained is washed with alcohol until perfectly white. It is then dissolved in enough water so that the hot solution is about half saturated, allowed to cool, and a little more than the required amount (2 molecules) of potassium hydroxide added. When cold, the addition of hydrochloric acid precipitates the acid potassium salt of orthosulphobenzoic acid in white plates. From the filtrate on evaporation more of the acid potassium salt can be obtained.

Fifty grams of the dried acid potassium salt are placed in a large mortar with 2.5 molecules of phosphorus pentachloride and the mixture intimately ground until reaction ensues. The resulting oil is then transferred to an evaporating dish, and placed on a steam-bath for several hours, until most of the phosphorus oxychloride has distilled off. It is then poured into a large bottle containing ice-water and shaken vigorously. After shaking with several changes of water it is ready for further use.

To obtain a mixture of the dry chlorides the oil is placed in a mortar with cracked ice and ground until it becomes solid. It is then filtered, washed with ice-water, and pressed between drying-paper, care being taken not to touch the product or have anything warm near it as the mixture melts at 21°. It is then dried in a desiccator in a cool place. One hundred grams of the mixed chlorides contain about 60 grams of the unsymmetrical chloride.

To obtain the symmetrical chloride the oil is at once dissolved in ether and transferred to a large separating funnel containing ice and water. Ammonia is then added, until after shaking for a few minutes the presence of ammonia is still detected. Hydrochloric acid is then added to neutralize the free ammonia, the ethereal solution washed, separated, and dehydrated with calcium chloride. On evaporating off the ether the chloride is obtained. This can be obtained perfectly

pure by crystallizing from pure ligroin (b. p. 90° to 125°).

The product melting at 21°, formerly considered to be the unsymmetrical chloride, has been shown to be a mixture of the two chlorides.[1] The pure unsymmetrical chloride melts at 40° and is prepared as follows: The neutral potassium salt of orthosulphobenzoic acid obtained by neutralizing the acid potassium salt with potassium hydroxide is heated in a sealed tube for four hours with 1.5 molecules of phosphorus oxychloride at 135°. The product is transferred to a mortar, ground up with several changes of ice-water, filtered, dried, and crystallized from pure ligroin. The yield is about 50 per cent.

A mixture of these chlorides has the property of crystallizing apparently as a chemical individual. It crystallizes in long radiating tufts, which melt at 21°, and is not changed by further crystallization.[2]

Chlorides of Paranitroorthosulphobenzoic Acid.—The symmetrical chloride of paranitroorthosulphobenzoic acid was prepared as described by Henderson.[3]

In the preparation of the unsymmetrical chloride, the method of Hollis[4] was not followed. A much better method of preparation was as follows: The neutral potassium salt of paranitroorthosulphobenzoic acid is heated with 1.5 molecules of phosphorus oxychloride in a sealed tube for four hours at 135°. The product is then transferred to a mortar, ground up with several changes of ice-water, filtered, dried, and recrystallized from pure ligroin. Only the unsymmetrical chloride was obtained and was identical with that described by Hollis. The reaction is a very clean one with a uniform yield of 50 per cent.

Action of Urea on the Chlorides of Orthosulphobenzoic Acid.

Action on the Symmetrical Chloride.—A mixture of the symmetrical chloride with urea in the proportion of 1 molecule of the former to 4 of the latter, was heated in a test-tube at various temperatures. When heated over a free flame or

[1] Ber. d. chem. Ges., 11, 1653 (1898).

[2] When certain investigations, now in progress in this laboratory, are completed, I shall have something further to say on this subject.—I. R.

[3] This JOURNAL, 25, 1.

[4] *Ibid.*, 23, 233.

above the melting-point of urea, violent reaction took place with a considerable evolution of heat. Hydrochloric acid was given off and biuret was formed. As the heat of the reaction was sufficient to destroy any excess of urea, no attempt was made to isolate the products.

When the mixture was heated at 100° the reaction proceeded very slowly and quietly without the evolution of heat. A mixture of the chloride and urea, in the proportion of 1 molecule to 4, was heated for several days at 100° in a test-tube. At first the mixture became liquid, forming two distinct layers. Stirring greatly facilitated the reaction. In the course of a few hours the mixture became pasty and stirring was necessary in order to insure a thorough mingling of the two constituents. At the end of two days the mass became hard. A little hydrochloric acid was given off during the experiment.

The hard cake formed was then dissolved in hot water. On cooling, a small quantity of a substance separated that was soluble in hot, but sparingly soluble in cold, water. This body contained no sulphur and appeared to be biuret. The mother-liquor, on concentration, yielded a very beautiful crystalline substance and small quantities of ammonium chloride. This substance had a strong crystallizing power and usually appeared in long, colorless, monoclinic prisms. It melted at 266°, was moderately soluble in water, but insoluble in alcohol or ether. It acted like an ammonium salt, giving off ammonia in the cold with weak alkalies. The yield was about 55 per cent of the theoretical and no other product was obtained.

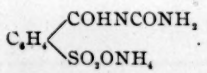
Action on the Unsymmetrical Chloride.—The same method of procedure was followed with the unsymmetrical chloride. The chloride with urea in the proportion of 1 molecule to 4 was heated in a test-tube at 100° for several days. Reaction took place much more quickly than with the symmetrical chloride. The resulting product was dissolved in hot water. On cooling, a small quantity of a substance separated that was soluble in hot, but sparingly soluble in cold, water. This body contained no sulphur and was identical with that obtained from the symmetrical chloride. From the mother-

liquor, on evaporation, the same characteristic, monoclinic prisms crystallized out that were obtained from the symmetrical chloride, and a small quantity of ammonium chloride. This substance melted at 266°, was moderately soluble in water, insoluble in alcohol or ether. It gave off ammonia in the cold with weak alkalies and was identical with the product obtained from the symmetrical chloride. The yield was about 55 per cent of the theoretical. On analysis it was found to have the following composition :

$$C_6H_4SO_3C_2H_7N_3.$$

	Calculated.	Found. I.	II.
C	36.75	36.61	36.70
H	4.22	4.29	4.28
S	12.27	12.31	12.38
N	16.14	16.34	16.10

It proved to be the *ammonium salt of benzoylureaorthosulphonic acid*,



Action of Hydrochloric Acid.—On boiling with dilute hydrochloric acid the ammonium salt was hydrolyzed to the acid ammonium salt of orthosulphobenzoic acid. This, when treated with potassium hydroxide, gave off ammonia, and, when acidified with hydrochloric acid, it gave the characteristic acid potassium salt of orthosulphobenzoic acid.

Action of Potassium Hydroxide.—The ammonium salt was boiled with a dilute solution of potassium hydroxide for six hours. Ammonia was constantly given off, showing a slow hydrolysis. On evaporating the solution the potassium salt of orthobenzaminesulphonic acid separated out. This salt was very soluble in water and crystallized in monoclinic plates. It contained 1 molecule of water of crystallization and was identical with the potassium salt of orthobenzaminesulphonic acid described by Remsen and Karslake.[1] This showed that the urea residue was in the carbonyl group.

[1] This JOURNAL, 18, 826.

0.1339 gram substance gave 0.0096 gram H_2O.
0.1546 gram substance gave 0.0111 gram H_2O.
0.2099 gram substance gave 0.0769 gram K_2SO_4.
0.1386 gram substance gave 0.505 gram K_2SO_4.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2OK} + H_2O$.	Found. I.	II.
H_2O	7.04	7.17	7.18
K	16.32	16.43	16.39

Action of Barium Hydroxide.—A solution of the ammonium salt was treated in the cold with an excess of barium hydroxide. Ammonia was given off, and after the solution had stood for some time the excess of barium hydroxide was removed by carbon dioxide. From the filtered solution, on evaporation, crystals of the barium salt of benzoylureaorthosulphonic acid separated out.

This salt was sparingly soluble in water and separated out in clusters of transparent, diamond-shaped crystals. It crystallized with 2 molecules of water of crystallization and effloresced on exposure to the air, becoming opaque.

0.3346 gram substance gave 0.0181 gram H_2O.
0.2109 gram substance gave 0.0110 gram H_2O.
0.1998 gram substance gave 0.0742 gram $BaSO_4$.
0.1972 gram substance gave 0.0732 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\langle^{COHNCONH_2}_{SO_2O}\right)_2Ba + 2H_2O$.	Found. I.	II.
$2H_2O$	5.47	5.40	5.22
Ba	21.98	21.82	21.80

Benzoylureaorthosulphonic Acid.—The free acid was made by treating the barium salt with an equivalent amount of sulphuric acid. It is a strong acid, extremely soluble in water, separating out as a silky mass only when the solution is evaporated to a thick syrup. No attempt was made to analyze it, and from a study of its salts its composition proved to be that represented by the formula

$$C_6H_4\langle^{COHNCONH_2}_{SO_2OH}$$

Potassium Salt.—This salt is moderately soluble in water, and separates out in especially well-defined, colorless, monoclinic prisms. It contains no water of crystallization and melts at 286°.

0.2406 gram substance gave 0.0740 gram K_2SO_4.

0.2465 gram substance gave 0.0753 gram K_2SO_4.

	Calculated for $C_6H_4\langle^{COHNCONH_2}_{SO_2OK}$	Found. I.	II.
K	13.85	13.80	13.71

Sodium Salt.—This salt separates out in thick, opaque, poorly defined prisms, apparently of orthorhombic habit. It is quite soluble in water, contains 1 molecule of water of crystallization, and effloresces on exposure to the air.

0.6932 gram substance gave 0.0430 gram H_2O.

0.5936 gram substance gave 0.0369 gram H_2O.

0.1826 gram substance gave 0.0486 gram Na_2SO_4.

0.2274 gram substance gave 0.0606 gram Na_2SO_4.

	Calculated for $C_6H_4\langle^{COHNCONH_2}_{SO_2ONa + H_2O}$.	Found. I.	II.
H_2O	6.33	6.20	6.22
Na	8.66	8.57	8.62

Lead Salt.—This salt is very soluble in water, separating out in clusters of thin, transparent, tabular plates. The crystals are not well defined, contain 3 molecules of water of crystallization, and effloresce on exposure to the air, becoming opaque.

0.5148 gram substance gave 0.0371 gram H_2O.

0.3417 gram substance gave 0.0254 gram H_2O.

0.1693 gram substance gave 0.0746 gram $PbSO_4$.

0.1742 gram substance gave 0.0770 gram $PbSO_4$.

	Calculated for $\left(C_6H_4\langle^{COHNCONH_2}_{SO_3}\right)_2Pb + 3H_2O$.	Found. I.	II.
$3H_2O$	7.25	7.20	7.43
Pb	29.85	30.00	30.05

Copper Salt.—This salt is moderately soluble in water, crystallizes in clusters of long blue prisms, and contains 6 molecules of water of crystallization.

0.1957 gram substance gave 0.0324 gram H_2O.
0.2585 gram substance gave 0.0422 gram H_2O.
0.2010 gram substance gave 0.0292 gram CuO.
0.2161 gram substance gave 0.0315 gram CuO.

	Calculated for $\left(C_6H_4\begin{matrix}COHNCONH_2\\SO_3\end{matrix}\right)_2Cu + 6H_2O$.	Found. I.	II.
$6H_2O$	16.45	16.60	16.33
Cu	11.52	11.59	11.62

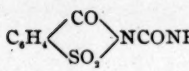
Silver Salt.—This salt was prepared by dissolving silver oxide in a solution of the free acid. It is moderately soluble in water, crystallizes in clusters of thick-pointed, poorly defined prisms, contains no water of crystallization, and darkens on exposure to the light.

0.2188 gram substance gave 0.0675 gram Ag.
0.2130 gram substance gave 0.0658 gram Ag.

	Calculated for $C_6H_4\begin{matrix}COHNCONH_2\\SO_3Ag\end{matrix}$.	Found. I.	II.
Ag	30.74	30.85	30.90

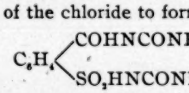
Several explanations of the formation of the ammonium salt of benzoylureaorthosulphonic acid suggest themselves. It is a secondary product formed after the heated mass had been dissolved in water. The hydrochloric acid in the aqueous solution decomposed the original compound with the formation of ammonium chloride. All attempts to isolate the original product failed. The mass of chloride and urea, after heating, was extracted with ether and chloroform, but nothing was obtained. This probably disproves the theory that the chlorine atom of the carbonyl group was acted upon and the chlorine of the sulphonyl group removed by subsequent hydrolysis. It completely dissolved in alcohol, showing that the ammonium salt was not the original compound. On account of its extreme solubility in alcohol or water and of its poor crystallizing power, it was impossible to separate it from the large amount of urea present.

There are two possible theories to account for the formation of the ammonium salt. One molecule of urea may have reacted with one molecule of the chloride to form a ureid,



which, on hydrolysis, would take up a molecule of water and give the free sulphonic acid. This, with the ammonium chloride formed from the decomposition of the urea hydrochloride, would give the ammonium salt.

On the other hand, two molecules of urea may have reacted with one molecule of the chloride to form a diureid,



The urea residue in the sulphonyl group was then hydrolyzed to the ammonium salt. This latter view seems the more probable.

Action of Urea on the Chlorides of Paranitroorthosulphobenzoic Acid.

Action on the Symmetrical Chloride.—As a rule, the derivatives formed from the chlorides of paranitroorthosulphobenzoic acid are less soluble than the corresponding derivatives formed from the chlorides of orthosulphobenzoic acid. In view of this fact, the action of urea upon these chlorides was tried to see if some of the intermediate products of the reaction could not be isolated.

A mixture of the chloride and urea in the proportion of 1 molecule to 4 was heated at different temperatures. When heated over a free flame or above the melting-point of urea violent reaction took place. Hydrochloric acid was given off and there was a considerable evolution of heat. As the heat of the reaction was sufficient to destroy any excess of urea no attempt was made to isolate the products.

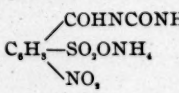
At 100° the reaction proceeded slowly and quietly without the evolution of heat. A mixture of the chloride and urea in the proportion of 1 molecule to 4, was heated for two days at 100°. At first the mass became liquid, forming two distinct layers. As the reaction proceeded stirring was necessary in order to insure a thorough mingling of the two constituents. Reaction took place more slowly than with the symmetrical chloride of orthosulphobenzoic acid.

The hard cake formed was dissolved in hot water. On cooling, a small quantity of a substance separated that was soluble in hot, but sparingly soluble in cold, water. It contained no sulphur and appeared to be biuret. The mother-liquor, on concentration, yielded small quantities of ammonium chloride and a well-crystallized substance of a pale-lemon color. This substance crystallized in diamond-shaped plates, and melted at 273°. It was moderately soluble in water, insoluble in alcohol or ether. It acted like an ammonium salt, giving off ammonia in the cold with weak alkalies. The yield was about 55 per cent and no other product was obtained.

Action on the Unsymmetrical Chloride.—The same method of procedure was followed with the unsymmetrical chloride. Reaction took place much more quickly than with the symmetrical chloride. The resulting product was dissolved in hot water. On cooling, a small quantity of a substance separated. This was soluble in hot, but sparingly soluble in cold, water. It was identical with that obtained from the symmetrical chloride and was probably biuret. From the mother-liquor, on evaporation, the same diamond-shaped plates separated that were obtained from the symmetrical chloride. These melted at 273°, were moderately soluble in water, insoluble in alcohol or ether. The substance gave off ammonia in the cold when treated with weak alkalies. It contained no water of crystallization and was identical with the product obtained from the symmetrical chloride. The yield was about 60 per cent. On analysis it gave the following results:

	Calculated for $C_8H_{10}O_7SN_4$.	Found. I.	II.
C	31.34	31.13	....
H	3.27	3.36	3.31
S	10.47	10.32	10.39
N	18.36	18.38	18.50

This substance proved to be the *ammonium salt of paranitrobenzoylureaorthosulphonic acid*,



Action of Fuming Nitric Acid.—The salt was boiled with fuming nitric acid to see if any nitroguanidine was formed, as would be the case if one of the urea molecules had acted upon a urea residue. Nothing but the acid ammonium salt of paranitroorthosulphobenzoic acid was formed. This salt crystallized in monoclinic plates, and was very soluble in water. On treating a solution of this salt with potassium hydroxide, ammonia was given off and, on acidifying, the characteristic acid potassium salt of paranitroorthosulphobenzoic acid separated out.

	Calculated for $C_6H_3(COOH)(SO_2ONH_4)(NO_2)$.	Found. I.	Found. II.
NH_3	6.43	6.39	6.38

Action of Hydrochloric Acid.—On boiling with dilute hydrochloric acid the ammonium salt was hydrolyzed to the acid ammonium salt of paranitroorthosulphobenzoic acid. It was identical with the salt obtained by the action of fuming nitric acid.

	Calculated for $C_6H_3(COOH)(SO_2ONH_4)(NO_2)$.	Found. I.	Found. II.
NH_3	6.43	6.51	6.41

Action of Potassium Hydroxide.—The ammonium salt was boiled with an excess of a dilute solution of potassium hydroxide for six hours. Ammonia was given off during the entire time, showing a slow hydrolysis. On concentrating the solution, the potassium salt of paranitroorthobenzaminesulphonic acid separated. This salt is very soluble in water, and separates in thin yellowish plates. It contains no water of crystallization.

0.1983 gram substance gave 0.0604 gram K_2SO_4.

0.2174 gram substance gave 0.0660 gram K_2SO_4.

	Calculated for $C_6H_3(CONH_2)(SO_2OK)(NO_2)$.	Found. I.	Found. II.
K	13.73	13.66	13.61

Action of Barium Hydroxide.—A solution of the ammonium salt was treated in the cold with an excess of barium hydroxide. Ammonia was given off and, after the solution had stood for some time, the excess of barium hydroxide was removed by carbon dioxide. From the filtered solution, on evaporation, crystals of the barium salt of paranitrobenzoylureaorthosulphonic acid separated. This salt crystallized in small, yellow prisms and was sparingly soluble in water. It contained two molecules of water of crystallization.

0.3815 gram substance gave 0.0178 gram H_2O.
0.3864 gram substance gave 0.0182 gram H_2O.
0.2778 gram substance gave 0.0906 gram $BaSO_4$.
0.1678 gram substance gave 0.0546 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}COHNCONH_2\\SO_3O\\NO_2\end{cases}\right)_2Ba + 2H_2O$.	Found. I.	II.
$2H_2O$	4.81	4.66	4.71
Ba	19.20	19.15	19.08

Paranitrobenzoylureaorthosulphonic Acid.—The free acid was made by treating the barium salt with the calculated amount of sulphuric acid. It is a strong acid, very soluble in water, separating out only when the solution is evaporated nearly to dryness. No attempt was made to analyze it.

Potassium Salt.—This salt has a marked crystallizing power, separating out in clusters of long, narrow prisms of a pale-yellow color. It is sparingly soluble in water and crystallizes with 1 molecule of water of crystallization.

0.3573 gram substance gave 0.0181 gram H_2O.
0.5992 gram substance gave 0.0312 gram H_2O.
0.3554 gram substance gave 0.0939 gram K_2SO_4.
0.2289 gram substance gave 0.0612 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}COHN.CONH_2\\SO_3OK\\NO_2\end{cases} + H_2O$.	Found. I.	II.
H_2O	5.22	5.07	5.21
K	11.94	11.85	11.97

Sodium Salt.—The sodium salt is moderately soluble in water and of a pale-yellow color. It has two habits of crystallization. When a solution of the salt is cooled quickly it

separates out in long silky needles, containing 4 molecules of water of crystallization. These give up water very quickly on exposure to the air. When the solution is cooled slowly the salt separates out in orthorhombic prisms containing 1 molecule of water of crystallization. The needles, on standing in the solution, slowly change to the orthorhombic prisms.

0.2893 gram substance gave 0.0158 gram H_2O.
0.2262 gram substance gave 0.0126 gram H_2O.
0.3311 gram substance gave 0.0615 gram H_2O.
0.2637 gram substance gave 0.0484 gram H_2O.
0.2292 gram substance gave 0.0520 gram Na_2SO_4.
0.1878 gram substance gave 0.0432 gram Na_2SO_4.

	Calculated for $C_6H_3(COHNCONH_2)(SO_2ONa)(NO_2)$	Found. I.	II.
H_2O	5.48	5.46	5.57
$4H_2O$	18.32	18.58	18.36
Na	7.39	7.33	7.40

Lead Salt.—This salt is quite soluble in water, separating out in thick, poorly defined prisms of a pale-yellow color. It crystallizes with 5 molecules of water of crystallization, and effloresces on exposure to the air.

0.1043 gram substance gave 0.0106 gram H_2O.
0.2115 gram substance gave 0.0216 gram H_2O.
0.1596 gram substance gave 0.0620 gram $PbSO_4$.
0.2394 gram substance gave 0.0932 gram $PbSO_4$.

	Calculated for $(C_6H_3(COHNCONH_2)(SO_2O)(NO_2))_2Pb + 5H_2O$	Found. I.	II.
$5H_2O$	10.31	10.16	10.21
Pb	26.38	26.50	26.56

Copper Salt.—This salt was made by dissolving freshly prepared copper oxide in a solution of the free acid. It crystallizes in small blue prisms, is quite soluble in water, and contains 3 molecules of water of crystallization.

0.1437 gram substance gave 0.0109 gram H_2O.
0.1314 gram substance gave 0.0102 gram H_2O.
0.2969 gram substance gave 0.0374 gram CuO.
0.1691 gram substance gave 0.0170 gram CuO.

	Calculated for $\left(C_6H_3\begin{cases}COHNCONH_2\\SO_3O\\NO_2\end{cases}\right)_2Cu + 3H_2O$.	Found. I.	II.
$3H_2O$	7.78	7.59	7.76
Cu	9.91	10.03	10.06

Silver Salt.—The silver salt was prepared by dissolving silver oxide in a solution of the free acid. It crystallizes in long, irregular prisms, is moderately soluble in water, and contains 1 molecule of water of crystallization. It darkens on exposure to light.

0.1531 gram substance gave 0.0064 gram H_2O.
0.1732 gram substance gave 0.0072 gram H_2O.
0.1622 gram substance gave 0.0444 gram Ag.
0.1438 gram substance gave 0.0392 gram Ag.

	Calculated for $C_6H_3\begin{cases}COHNCONH_2\\SO_3OAg\\NO_2\end{cases} + H_2O$.	Found. I.	II.
H_2O	4.34	4.18	4.16
Ag	27.27	27.37	27.25

The ammonium salt of paranitrobenzoylureaorthosulphonic acid is a secondary product formed after the heated mass had been dissolved in water. The hydrochloric acid in the aqueous solution probably decomposed the original compound with the formation of ammonium chloride. All attempts to isolate the original compound failed. The mass of chloride and urea, after heating, was extracted with ether and chloroform, but nothing was obtained. It completely dissolved in alcohol, showing that the ammonium salt was not the original compound. It was deliquescent and very soluble in alcohol or water. No intermediate products of the reactions could be isolated.

There are two possible theories to account for the formation of the ammonium salt, as in the case of the ammonium salt of benzoylureaorthosulphonic acid. One molecule of urea may have reacted with 1 molecule of the chloride to form a ureid,

$$C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NCONH_2,$$

which, on hydrolysis, would take up a molecule of water and give the free sulphonic acid. This, with the ammonium chloride formed from the decomposition of the urea hydrochloride, would give the ammonium salt.

The other explanation is that 2 molecules of urea may have reacted with 1 molecule of the chloride to form a diureid,

$$C_6H_3\begin{cases}\diagup COHNCONH_2\\ —SO_2HNCONH_2.\\ \diagdown NO_2\end{cases}$$

The urea residue in the sulphonyl group is then hydrolyzed to the ammonium salt. This view seems the more probable.

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Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXX.—ON THE NATURE OF LEAD AMALGAMS.

By Henry Fay and Edward North, 2nd.

Some time ago Gressman[1] published an article on "The Electrical Resistance of Lead Amalgams at Low Temperatures," in which he came to the conclusion that lead and mercury form a series of amalgams in which there is a eutectic alloy. He used amalgams containing from 4 to 25 per cent of mercury and determined the following freezing-points:

Pure mercury	—38°.8
4.2 per cent lead	—37°.7
7.1 " "	—37°.0
11.2 " "	—30°.0
Viscid, 25.0 per cent lead	—37°.65
Eutectic	—40°.0

These points were obtained by measuring the electrical resistance, and calculating from this the temperature at the moment of solidification, which was indicated by a sudden and marked increase in the conductivity of the amalgam as it passed from the liquid to the solid state. The points obtained by Gressman, plotted in the form of a curve, are shown in Fig. 1, in which abscissas represent percentage composition, and ordinates temperatures of freezing.

[1] Phys. Rev., 9, 20.

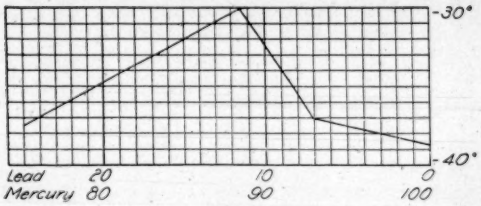

Fig. 1.

It seemed improbable that the mercury-lead amalgams should have such a fusibility curve if the amalgams are in any respect analogous to alloys, which have been shown to be analogous in their behavior to solutions. It is seen that the curve rises to a maximum at 11.2 per cent lead, which would seem to indicate a compound at that point. It then falls rapidly to the 25 per cent amalgam, indicating that it was falling toward a eutectic point. The percentage composition of the eutectic was not given, consequently its point could not be included in the curve. Gressman prepared his eutectic alloy by freezing out part of the amalgam, and then pouring off the portion remaining liquid. It is natural to suppose that in the process of freezing, the lead would separate first, which would, accordingly, concentrate the mercury. If this is actually the case, the percentage of mercury would probably be greater than 75 per cent, and the eutectic point would fall somewhere in the field already plotted. Assuming that the points already plotted are correct, he should have obtained two separate freezing-points for some of his amalgams, one of which would represent the separation of pure lead, pure mercury, or compound, and the other the separation of the eutectic. No such phenomena were observed. With alloys which form eutectic mixtures, and solutions which form cryohydrates, these two points of solidification are very evident. On the other hand, the statement is made that "usually the more lead the amalgam contains, the lower is the melting-point." The direction of the fusibility curve would indicate a minimum point at about 30 per cent lead. This should, then, be about the composition of the eutectic alloy, although the ex-

periments seem to indicate that the eutectic was much richer in mercury. If the eutectic contained as much as 30 per cent of lead, it would be more or less solid at room temperature, which could hardly be expected of a substance melting as low as —40°.

In consideration of the doubt in regard to these points and to the many conflicting statements in the literature in regard to the nature of the amalgams, it was decided to study the subject anew, and to apply those methods which have been of such great value in clearing up the nature of alloys, *viz.*, the establishment of the curve of fusibility, or, what is practically the same thing, the solubility curve, by determining the freezing-points of the amalgams by means of the LeChatelier pyrometer, and the study of the microstructure of the solid amalgams.

The determination of the freezing-point of amalgams by means of the pyrometer is not nearly so satisfactory as it is for alloys on account of their lack of crystalline character. With pure metals, and alloys which are to any extent crystalline, the point of solidification is very clearly marked, but with amalgams the deflection of the galvanometer is not so well marked. When readings of the galvanometer are taken every ten to twenty seconds, the cooling curve shows a retardation at the point of solidification, which cannot be mistaken. The evidence obtained from a study of the microstructure supplements that obtained by an inspection of the fusibility curve.

The fusibility curves of alloys have been found to fall under three general classes:

I. Two metals which form solid solutions give a straight line curve connecting the two melting-points. Examples of this class are the alloys of silver and gold, and bismuth and antimony.

II. Two metals which neither form solid solutions nor compounds, give a two-branch curve meeting in a eutectic point, which is lower than the melting-point of either metal. Typical examples of this class are the alloys of tin with bismuth, lead, and zinc, and the alloys of zinc with aluminium, and cadmium.

III. Two metals which form one or more compounds give

a curve, the number of branches of which is $2n + 1$ where n represents the number of compounds. In this class one of the compounds may form a solid solution with one of the pure metals, which would, consequently, modify the character of the curve, and therefore change the number of branches. Examples of this class are the alloys of copper with antimony, tin, and bismuth; those of aluminium and gold, antimony and zinc, and tin and nickel.

The study of the microstructure of these three classes of alloys confirms very decisively the fusibility curves. In the first class it is known that the solvent and dissolved substance separate out together. The microstructure of metals which form solid solutions shows a homogeneous mass in which it is difficult, if not impossible, to distinguish between the two constituents. In the second class, where the freezing-point of the pure metal is considerably lowered by the addition of the other metal, we know that there is first a separation of pure solvent, and as the temperature of the solution is lowered the pure metal continues to separate until the concentration of the resulting solution has reached that of the eutectic alloy when the mass solidifies as a whole. The microscopic constituents, consequently, should be pure metal and the eutectic, the amount of each depending upon the proportion of the two constituents. As the eutectic is the alloy in which the two constituents are each saturated with the other and the two separate simultaneously, we should expect to find a structure made up of alternate layers of the two metals. This is actually found to be the case, and the structure for all eutectics is very characteristic, resembling the fine line markings of the thumb. The eutectic may consist of two metals, a metal and a compound, or two compounds, but in all cases its structure is very characteristic and easily recognized. The presence of compounds in the third class is usually recognized by their crystalline form, the forms of some of them being very characteristic, such as is the case for the compound $SnCu_4$. When, however, a compound forms a solid solution, the detection of the two constituents is much more difficult.

In regard to the existence of compounds in amalgams there is a great variety of statement, and the evidence of their exis-

tence is based on a number of methods of investigation, most of which are unsatisfactory. By studies of the specific gravity, specific heat, heat of formation, heat of solution, effect of pressure, and electrical conductivity, the existence of a number of compounds of mercury with the metals is said to have been established, but only in a few cases is the evidence at all conclusive. With more refined methods of investigation, many of the so-called compounds will undoubtedly disappear.

Joule[1] applied a pressure of three tons to the square inch for a day to an amalgam of lead and mercury and obtained a bright crystalline mass, which corresponded closely to the formula Pb_3Hg. Croockewit[2] treated different amalgams with dilute acids and analyzed the portions remaining undissolved. In many cases the results of the analyses agreed closely with the percentages required for certain compounds. For lead amalgams he obtained a residue which corresponds to the composition required by the compound PbHg. Bauer[3] allowed acetic acid and carbon dioxide to act upon an amalgam composed of 2 parts lead and 1 part mercury until neither lead acetate nor lead carbonate were formed. The residue was hard, crystalline, and white. It changed to a bluish-yellow color when exposed to the atmosphere. The composition corresponded to the formula Pb_2Hg_3. Kasantseff[4] studied the action of nitric acid on solid and liquid gold amalgams. He found that the residues which remain do not possess a homogeneous composition, which led him to the supposition that there probably exist hydrargyrates dissolved in mercury, corresponding to the hydrates dissolved in water. The amalgams of gold, lead, and silver were subjected by De Souza[5] to the vapors of boiling mercury, sulphur, and diphenylamine, and they were kept at these temperatures until constant weight was obtained. When heated in boiling sulphur, the residues corresponded to the composition Au_6Hg, $Ag_{13}Hg$; heated in boiling mercury vapor, the residues corresponded to Au_9Hg, $Ag_{11}Hg$, Pb_8Hg; heated in the vapor of diphenylamine the

[1] J. Chem. Soc., **16**, 378.
[2] J. prakt. Chem., [1], **45**, 88.
[3] Ber. d. chem. Ges., **4**, 449.
[4] Bull. soc. chim., [2], **30**, 20.
[5] Ber. d. chem. Ges., **8**, 1616; **9**, 1050.

residues were Au_4Hg and Ag_4Hg. Lead, zinc, cadmium, and bismuth amalgams still retained mercury at 360°, but not at 440°. The experiments of De Souza were repeated by Merz and Weith,[1] who modified his methods to some extent, but they were unable to confirm his results. Amalgams were heated for many hours in the vapors of sulphur, mercury, and diphenylamine, carbon dioxide being passed over the amalgams during the heating. The results in nearly all cases gave no evidence of the existence of definite compounds. The gold, silver, copper, bismuth, lead, zinc, and cadmium lost their mercury entirely, or nearly so, at, or in some cases below, the boiling-point of mercury. With those amalgams in which small amounts of mercury were left behind, it was attributed more to mechanical action than to the formation of definite compounds. The most strongly pronounced evidence of chemical compounds was shown by the sodium and potassium amalgams, which lost their mercury only very slowly at the boiling-point of sulphur. On the other hand, as Merz and Weith show, the easy decomposition of the amalgams is not positive proof that compounds do not exist. More positive evidence was obtained in favor of compounds in the amalgams of sodium and potassium by determinations of the melting-points. With sodium they obtained a maximum point with 4.7 per cent of sodium, which melted at 305° to 315°; with potassium, at 9.8 per cent, a maximum was obtained at 240° to 245°. Increase of sodium or potassium lowered the melting-point again.

Tammann[2] has pointed out the close relationship between solutions and amalgams, and shows that if on solidification the pure solvent separates, the freezing-point will be lowered, while, on the other hand, if the two constituents separate together, the freezing-point will be higher than that of the solvent. In case of solid solutions the two constituents separate together and the curve of fusibility will connect the two melting-points of the constituents by a straight line. Mazzotto[3] points out the analogy between amalgams and alloys, and shows that while they are similar in most respects

[1] Ber. d. chem. Ges., 14, 1438.
[2] Ztschr. phys. Chem., 3, 440.
[3] *Ibid.*, 13, 571, 572.

their behavior is not identical. They show, on cooling, the various stages, just as alloys do, *viz.*: 1. The mass cools evenly and remains homogeneous and perfectly fluid; 2. The rate of cooling decreases, and at the same time solid particles separate out in the alloy, and increase in number as the temperature falls; 3. The temperature remains constant and the mass solidifies as a whole; 4. The mass again cools evenly. In the second stage Mazzotto finds that pure metals separate from zinc, lead, and bismuth amalgams, while sodium and cadmium deposit solid amalgams of variable composition. As we have not been able to obtain the original paper, it is impossible to state how it was proved that pure metal separates. Mazzotto points out, and it is confirmed by our experiments, that the stop in the third stage of cooling does not take place at a temperature below the freezing-point of the pure metals, as in the alloys, but at the freezing-point of mercury, from which it may be concluded that at this temperature practically no metal remains in solution in the mercury. An exception was found in sodium amalgam which seems to have a eutectic, composed of 5 parts of sodium and 20 parts of mercury by volume, which freezes at —46°. The third stage may be entirely absent in the case of those amalgams which form compounds.

Recently Puschin[1] has constructed some fusibility curves founded on empirically obtained data, and has come to the conclusion that the amalgams of lead, tin, bismuth, cadmium, and zinc, are all very similar in their nature. He says that none of them seem to show a well-established eutectic point, nor a maximum point indicating a compound. The lowering of the temperature of solidification was found to take place uniformly and uninterruptedly, passing from the heavy metal to mercury. According to Puschin the character of the curve shows that the amalgams of lead, tin, bismuth, zinc, and cadmium form isomorphous mixtures (solid solutions), the varying composition of which is dependent upon the temperature of the separation of the solid phase, and that the formation of such compounds as $HgPb_2$, $HgBi_2$, Hg_2Zn_3, and Hg_3Cd, as described in the literature, is doubtful. Puschin promises to

[1] Russ. Phys. Chem. Soc., **32**, 635; Chem. Ztg., **24**, 950.

publish later the experimental data of his work, and until then we cannot speak critically of his conclusions, but as the present work has been completed for some time, and has been held back, awaiting the results of some experiments on gold amalgams, we have decided to publish this preliminary paper principally because we have reached different conclusions, having used the same method of experimentation.

The results of our experiments seem to show that in the amalgams of lead and mercury there exists the compound Pb_4Hg, which is soluble in and isomorphous with lead, and it consequently lowers the freezing temperature of lead, as it is

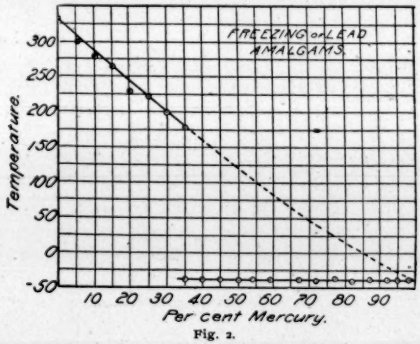

Fig. 2.

successively added to it. This compound is insoluble in mercury and hence does not lower the freezing-point of mercury. The results of the experiments seem to disprove conclusively the statement of Gressman that lead and mercury form a eutectic mixture. This is shown by the absence of any eutectic point in the fusibility curve, and also by the microscopic examination. Reference to Fig. 2, in which the freezing-points have been plotted, the abscissas representing composition and the ordinates temperatures, will show that the lower freezing-points all fall along a straight line drawn slightly above the melting-point of pure mercury.

The four exceptions which lie below this line occur at wide

intervals from each other, and their discrepancy is probably due to slight experimental errors, caused in the variations of the galvanometer from day to day. The existence of a eutectic alloy would have been indicated by a downward slant of the lower branch of the curve, its composition being determined by the point at which the two branches intersected. The lower branch is, however, horizontal.

Another argument against the non-existence of a eutectic alloy is the great similarity in appearance of the microstructure of all the solid amalgams. This includes examination only of those amalgams under 30 per cent of mercury, and on this account the evidence is not entirely satisfactory. The presence of a eutectic, even in small quantities, could hardly fail to make considerable change in the appearance of the structure, especially so if Gressman's statement is true that with increase of lead the freezing-point is lowered. Again, no alloy thus far examined possesses a eutectic freezing at a temperature less than 5° below the freezing-point of its most fusible constituent. Gautier[1] reports several alloys, such as those of lead and copper, nickel and tin, lead and aluminium, and antimony aluminium, in which the melting-point of the eutectic is within a few degrees of the more fusible metal. In the case of lead copper alloys with 0.14 per cent of copper, the melting-point of lead is lowered 2°, while with 0.31 per cent it is raised 4° above the melting-point of lead. This lowering of the melting-point can easily be accounted for by the presence of a small amount of impurity in the lead, and further and more careful study of pure metals will probably show these results to be inaccurate, and the eutectics with melting-points so close to that of the pure metal, which now appear in the alloys named, will disappear. This, of course, does not preclude the possibility that lead and mercury may form a eutectic freezing at 2° below the freezing-point of mercury, but there is little evidence to show that such is the case, while the evidence to the contrary is strong.

It will be seen from Fig. 2 that the higher freezing-points, so far as determined, lie along a straight line, which, if continued as indicated by the dotted portion, would meet the

[1] Bull. de la Société d'Encouragement, [5], 1, 1393.

lower horizontal branch at a point corresponding to the freezing of pure mercury. Such a curve, if considered by itself, is that of a solid solution, the freezing-points of which lie along a line connecting the freezing-points of the constituent metals. This portion of the curve may equally well represent the solubility of mercury in lead, and it is seen that up to about 35 per cent of mercury, the freezing-point of lead is successively lowered by the addition of mercury. From the nature of the lower branch it would appear that lead, on the contrary, is not soluble in mercury, and consequently has no effect on the freezing-point of mercury. The solubility of lead in mercury has been determined by Gouy,[1] who found it to be 0.013, which is very small. As will be shown later, this value probably also represents the solubility of the compound Pb_3Hg, the value for which would be 0.018.

The nature of the curve is so unusual and so different from any that have heretofore been established, that we have been in some doubt in regard to its explanation, but if we assume the existence of the compound Pb_3Hg and that this compound is only slightly soluble in mercury, the explanation appears to be simple, and, furthermore, is supported by the facts and the general behavior of the amalgams. According to this assumption, the upper branch of the curve shows that the compound is soluble in lead, and lowers its freezing-point as it is formed in larger and larger quantities, with the increase in the amount of mercury.

The microstructure seems to indicate that the two substances are isomorphous, for there is no separation into constituents visible on etching the solid amalgam.

When the percentage of mercury has reached 32.58 per cent there is nothing present but pure compound. If the percentage of mercury is now increased, there is more than enough present to form the compound Pb_3Hg, and mercury becomes the solvent. As the compound is only slightly soluble in mercury, it can have little or no effect upon the freezing-point, and consequently the freezing-points obtained are practically those of pure mercury. They are all slightly above the freezing-point of mercury, with the exception of a few previously men-

[1] J. de Physique, 4, 320.

tioned, which would be expected, as the mercury is probably supersaturated with the compound.

That the compound is insoluble in mercury receives further confirmation from the fact that by pressure Joule obtained a residue which corresponded to the compound Pb_4Hg. All lead amalgams, which are more or less liquid at room temperatures, contain solid particles which may readily be seen. By pressure always the same amalgam is obtained, which, after melting, consists of a crystalline mass in which the edges of the small crystals are rounded off on account of being wetted by the slight excess of mercury. The removal of the mercury which is in excess of that to form the compound Pb_4Hg, may be nicely accomplished by rotating in a centrifugal machine small chamois bags containing liquid amalgam. Under these conditions the excess of mercury is easily removed and the nearly pure compound is left in the bag. An examination of the mercury thus removed shows only traces of lead dissolved in it.

It was not possible to obtain this compound absolutely pure, but the results of a number of analyses show percentages of lead, varying from 66 to 68 per cent. The theoretical percentage is 67.42 per cent lead. Some of the mercury is mechanically held, which make the determinations of lead slightly low.

It will be seen that these phenomena are very similar to those observed in ordinary solutions containing a slightly soluble substance. The solvent, in this case mercury, on account of its great viscosity, is much more difficult to remove completely. Ordinary solvents, however, on account of their extreme limpidity may be easily removed by filtration. Mercury can be separated if sufficient pressure is used. The process of filtering mercury is carried on to a large extent in the gold amalgamation process where the mercury is pressed through buckskin bags, leaving behind a compound of mercury and gold. We have very good evidence that a compound of the formula $AuHg_4$ exists, and perhaps another, the composition of which has not yet been established.

The separation of a compound isomorphous with one of the constituents has a parallel in the field of solutions. Rooze-

boom has found that the double chloride of ammonia and ferric iron is isomorphous with ammonium chloride, and Le Chatelier has obtained the compound AgCl.NaCl isomorphous with sodium chloride, and the compound $2Na_2SO_4.CaSO_4$ isomorphous with sulphate of sodium. The isomorphism of Pb_3Hg with lead is entirely analogous.

Experimental.

Twenty-one lead amalgams were prepared in which the per cent of lead varied from 2 to 95 per cent. Pure sheet lead, prepared for use in assaying, and chemically pure mercury were used. In making an amalgam, the lead and mercury were weighed to the nearest 0.1 gram, the lead was melted in an annealing cup, the small amount of oxide skimmed off, and the mercury poured in just as the lead began to harden. The amalgam was then thoroughly stirred with a glass rod.

None of the amalgams which contain more than 35 per cent of mercury are entirely liquid. They consist of a liquid and of a pasty, granular, or semisolid portion, which can be easily separated from the liquid part by filtering the amalgam through chamois skin. If considerable pressure is applied, so as to remove all the liquid, or if the liquid is removed by means of a centrifugal machine, there remains a hard, silvery-white amalgam, which is brittle, has a bright granular fracture, and is easily oxidized to a bluish-yellow on exposure to the air. The solid constituent of the amalgams increases in quantity as the percentage of lead increases, and if it does not form too large a proportion of the amalgam, it can apparently be dissolved in the liquid portion by shaking. This, however, is only apparent, as the excess of mercury can readily be removed. On heating, the solid constituent goes into solution, and the temperature at which this takes place is higher as the percentage of the solid increases. These semisolid amalgams are very similar in their behavior to a slush composed of snow and water, from which the liquid portion, water, can be removed by pressure, leaving the more solid ice behind. An amalgam containing about 65 per cent lead is entirely solid. Further addition of lead causes a gradual change from the silvery-white amalgam to the bluish-gray color of

pure lead, accompanied by a corresponding increase in the malleability, and a disappearance of the granular fracture.

Cooling and warming curves were run for nearly all of the amalgams. The cooling curves cover the range from the temperatures at which the amalgams are entirely liquid down to room temperature. The warming curves start below the melting-point of mercury and extend to room temperature. The temperatures were measured by means of a thermoelectric couple in connection with a galvanometer of the suspended coil or d'Arsonval type. The junction, composed of a platinum and a platinum-rhodium wire, was protected by a thin piece of hard glass tubing, about 2 mm. in diameter. Inside this tube the wires were insulated by passing over one a fine piece of tubing drawn down from a larger size. The cold junction was enclosed in a bottle surrounded by hair-felt. A thermometer with its bulb in the bottle gave the temperature of the cold junction to 0.1°. The suspended coil of the galvanometer carried a mirror throwing a beam of light on a millimeter scale. The shadow of a vertical wire was read to the nearest 0.1 mm. A scale deflection of 1 mm. was equivalent to a rise or fall in temperature of about 3°. Theoretically, it should have been possible to determine temperatures within 0.3°, but such a degree of accuracy was not practically obtainable. More than half of the freezing-point determinations were made at or near the freezing-point of mercury, and it was highly essential that the results should be reliable, as a variation of a few degrees above or below this temperature, in the freezing of any of the amalgams, might lead to entirely different conclusions. What appeared to be discrepancies, often amounting to 3° or 4°, were noticed in the first series of determinations. Investigation showed that the galvanometer was apt to vary from day to day, the deflection at the temperature of melting mercury often changing by several degrees from one day to the next. It was, therefore, found necessary, in order to obtain satisfactory results, to redetermine the melting-point of mercury three or four times each day, and calculate the freezing-point of each amalgam from the calibration last made. Before and after each experiment the temperature of the cold junction was noted, and the zero reading of the galvanometer, after breaking the circuit.

The galvanometer was calibrated by exposing the couple to the vapors of boiling water (100°), boiling naphthalene (218°.7), and boiling aniline (182°.6) and by placing it in melting mercury (—39°.4). In measuring temperatures below the room temperature the galvanometer connections were reversed in order to give a positive deflection instead of a negative deflection, as would otherwise have been the case.

In order to freeze the amalgams a mixture of ether and solid carbon dioxide was used. The carbon dioxide was obtained in the form of snow by winding a heavy Canton flannel cloth around the orifice and top of a cylinder of the liquefied gas. The tank was laid on its side and the valve opened wide. A few moments sufficed to collect a large amount of snow. This was placed in a beaker surrounded by hair-felt, the whole enclosed in a thick cylinder of cork. Ether was slowly added till the mixture had the consistency of slush. The amalgam, contained in a test-tube, with the thermoelectric couple in its center, was placed in the mixture till frozen solid. When the amalgam was cooled to —75°, the temperature of the freezing mixture, it was quickly removed and placed in a second larger test-tube, so that it was surrounded by an air jacket, and warmed slowly and evenly until room temperature was reached. The warming of the amalgam occupied about twenty minutes, and during this time galvanometer readings were taken every ten seconds.

The solid amalgams, which have a second or higher melting-point, were melted in a small electric furnace made of a porous cup wound with iron wire, the whole surrounded with asbestos and sheathed with wood. When the amalgam was melted the current was shut off and the amalgam allowed to cool slowly in the furnace. Galvanometer readings were taken at intervals of twenty seconds.

The semiliquid amalgams became entirely fluid at comparatively low temperatures (under 150°), and the electric furnace, owing to its size, cooled very slowly at these low temperatures. Therefore, such amalgams were transferred from the freezing mixture to a bath of sulphuric acid, and heated until entirely liquid. For such amalgams only one curve, a warming curve, was plotted, which covers the entire range

from a temperature beyond the lowest freezing-point up to one at which the amalgam is entirely liquid. Two amalgams, numbers 9 and 10, were, in addition, melted and cooled in the electric furnace.

The freezing-points of the lead amalgams are given in the following table and are represented graphically in Fig. 2 (p. 223).

Freezing-points of Lead Amalgams Shown Graphically in Fig. 2.

No.	Per cent lead.	Lower freezing-point.	Upper freezing-point.
1	2	—39°.0	
2	5	—39°.0	
3	7	—40°.6	
4	13	—38°.9	
5	18	—42°.0	
6	23	—37°.6	
7	28	—40°.9	
8	33	—39°.0	
9	65.3	—37°.4	185°.2
10	40.8	—39°.1	
11	46	—37°.8	
12	50	—39°.0	
13	55	—39°.6	
14	60	—40°.2	
15	65	—37°.8	177°.3
16	70		199°.4
17	75		221°.0
18	80		229°.0
19	85		263°.7
20	90		278°.5
21	95		299°.3

The results show that the lead amalgams freeze at about the same temperature as pure mercury until the amount of lead reaches 65 per cent. Beyond this point the lower freezing-point disappears, or becomes so indefinite that it does not show, and the amalgams solidify at a temperature which is higher in proportion to the increase in the percentage of lead. Amalgams 9 and 15 possess the upper and lower freezing-points, which may be accounted for by the fact that they are not entirely homogeneous, which is more or less true of all of the amalgams. It will be seen that, with four exceptions, the amalgams having the lower freezing-point all melted at a

temperature slightly above the melting-point of pure mercury. These exceptions are widely separated, and are probably due to unavoidable inaccuracies in the temperature measurements caused by the variations of the galvanometer.

In order to examine the solid amalgams under the microscope it was necessary to polish them to a mirror surface. There was considerable difficulty in polishing the amalgams on account of the strong tendency of the mercury to smear the surface when the least pressure was exerted. A mirror surface could, however, be obtained when the surface was first made roughly plane by filing, and then rubbed lightly on a whetstone under water until the file marks disappeared, the final polish being done on wet chamois covered with jeweler's rouge. The most convenient method of obtaining a mirror surface was obtained by casting the melted amalgam on plate glass. This gave a surface which was entirely free from marks and gave a beautiful mirror ready for examination. Numerous etching agents were tried in the endeavor to make a sharp distinction under the microscope between the lead and the mercury. The appearance varied considerably with the different etching agents, but in no case was there a separation into two constituents, as would be expected if lead had separated as pure solvent or if there had been a eutectic mixture. The structure in all cases showed the same general characteristics, becoming coarser as the percentage of mercury increased. The 65 per cent amalgam showed very well developed grains, showing the crystalline nature of the amalgam. The outlines of the grains, however, gave no clue to the crystal system. The different amalgams were compared with some alloys which were known to give isomorphous mixtures, and in general appearance it was difficult to distinguish between them.

Other amalgams are now being studied in this laboratory, and it is hoped that work along similar lines will throw some light on the nature of the amalgams of gold, silver, tin, zinc, and bismuth, concerning which our present knowledge is unsatisfactory.

BOSTON, January 12, 1901.

REPORT.

The Dissociating Power of Different Solvents. A Summary.

The question of the dissociating power of different solvents is one of the most important in physical chemistry today. The first step in the study of the physical chemistry of any solvent is to determine accurately its dissociating power, in order that the knowledge obtained may not be simply qualitative but quantitative.

It has often been pointed out that physical chemistry, until quite recently, was almost exclusively the physical chemistry of aqueous solutions. This is due to the fact that water is a good solvent for many substances, that it can be easily obtained in a high degree of purity and kept free from other solvents, and further, that the dissociating power of water can be easily measured. In the last few years, however, a beginning has been made with other solvents, and the first step—the measurement of their dissociating power—taken, at least approximately in a number of cases.

The question of the dissociating power of solvents has acquired additional interest because of certain theories which have been proposed, connecting this property of solvents with other properties, chemical and physical. Thus, J. J. Thomson,[1] and also Nernst,[2] have proposed the theory that the dissociating power of solvents should be very closely connected with their dielectric constants. Brühl[3] thinks that water and similar substances are non-saturated compounds, and refers the large association of their molecules (shown by the surface-tension method of Ramsay and Shields), as well as their large dielectric constant and high dissociating power, to this cause. Ciamician[4] thinks that dissociation is a chemical function of the substance, and those compounds which resemble one another chemically, as water, methyl alcohol, etc., should have the greatest dissociating power. While Konowalow[5] holds the opinion that only those solutions conduct where there is a chemical action between the solvent and the dissolved substance.

The work which has been done will be considered under

[1] Phil. Mag., **36**, 320.

[2] Ztschr. phys. Chem., **13**, 531.

[3] *Ibid.*, **18**, 514; **27**, 319; **30**, 1; Ber. d. chem. Ges., **30**, 163; **28**, 2847; and **28**, 2866.

[4] *Ibid.*, **6**, 403.

[5] Wied. Ann., **49**, 733.

the following heads: Inorganic solvents, organic solvents, and mixed solvents.

Inorganic Solvents.

Water.—The dissociating power of water has been determined for a large number of substances, by several different methods. The more general methods are: The conductivity method of Kohlrausch,[1] the solubility method of Nernst[2] and Noyes,[3] and the freezing-point methods of Jones,[4] Loomis,[5] and others.

The results obtained by all of these methods agree to within the limit of experimental error. Water, as we shall see, has the highest dissociating power of any solvent thus far obtained in the pure state, and it is probable that there is only one other substance known which, under similar conditions, can ionize substances to the same extent as water.

To determine the dissociating power of solvents other than water, the conductivity method has thus far been chiefly used. In order that the conductivities in other solvents may be compared with those in water, the results for a typical acid, base and salt in aqueous solution are given. The following measurements were made at 18°. The volume v is the number of liters which contains a gram-molecular weight of the electrolyte. μ_v is the molecular conductivity at the volume v.

Hydrochloric acid.		Potassium hydroxide.		Potassium chloride.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
0.1	60.0	0.1	42.3		
0.2	142.0	0.2	99.0		
0.333	201.0	0.333	131.4	0.333	82.7
1.0	278.0	1.0	171.8	1.0	91.9
10.0	324.4	10.0	198.6	10.0	104.7
100.0	341.6	100.0	212.4	100.0	114.7
500.0	345.5	500.0	214.0	500.0	118.5
1000.0	345.5	1000.0	213.0	1000.0	119.3
				5000.0	120.9
				10000.0	120.9

The percentage of dissociation, α, at any dilution is obtained by dividing the value of μ_v at that dilution by the maximum value of μ_v for the substance, which is called μ_∞.

In most solvents it is impossible to determine the value of

[1] Wied. Ann., **26**, 160.

[2] Ztschr. phys. Chem., **4**, 372.

[3] *Ibid.*, **6**, 241; **9**, 603; **12**, 162; **16**, 125.

[4] *Ibid.*, **11**, 110, 529; **12**, 623.

[5] Wied. Ann., **51**, 500; **57**, 495, 591; **60**, 523.

μ_∞ directly by the conductivity method, since the dilution at which μ_∞ is reached would be so great that it would not be practicable to apply the conductivity method to it. The best that can be done in such cases is to determine the values of μ_v for varying dilutions and then compare these with the corresponding values in water. In this way an approximate idea of the dissociating power of different solvents can be obtained.

Ammonia.—That solutions of salts in liquid ammonia conduct the current was shown several years ago by Cady.[1] Goodwin and Thompson[2] also made some measurements of the conductivity of such solutions, in connection with their work on the dielectric constant of liquid ammonia, but the most elaborate investigation in this field is that of Franklin and Kraus.[3] They measured the conductivity of potassium bromide and nitrate, sodium bromide and bromate, ammonium chloride and nitrate, silver iodide and cyanide, mercuric cyanide, and a number of organic compounds in liquid ammonia, at dilutions ranging from a few hundred to many thousand liters. A few of their results for three salts are given :

Potassium bromide.		Ammonium chloride.		Silver iodide.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
301.9	210.6	298.9	159.0	314.1	83.5
932.6	259.5	923.4	208.7	951.3	122.7
4099.0	308.5	4059.0	264.7	4034.0	188.2
21480.0	336.1	21270.0	298.8	18200.0	247.5
65040.0	340.2	64400.0	301.4	55120.0	274.0
78430.0	340.4	77660.0	304.4	80000.0	276.0

A direct comparison of the molecular conductivities of salts in liquid ammonia with the molecular conductivities in water at the same dilutions, will show that the former values are much larger than the latter. This would seem to indicate, at first sight, that ammonia has a greater dissociating power than water, but such is not the case. It will be observed that the conductivities in water are measured at 18°, or 82° below its boiling-point, while the conductivities in liquid ammonia are measured at its boiling-point —38°. The conductivities in liquid ammonia should be compared with the conductivities in water at its boiling-point, and the latter values would be, in many cases, more than double the conductivities in water at 18°.

Further, if the molecular conductivities in liquid ammonia

[1] J. Phys. Chem., 1, 707.
[2] Phys. Rev., 8, 38.
[3] This JOURNAL, 23, 277; 24, 83.

should even be greater than in water under comparable conditions, this alone would not show that the dissociating power of ammonia was greater than that of water. The percentage of dissociation, $\alpha = \frac{\mu_v}{\mu_\infty}$. μ_v might be larger in ammonia than in water, and the difference between the two values of μ_∞ might be even greater, so that μ_∞ would be smaller in ammonia. Such is the fact. The high value of the molecular conductivity in ammonia is due rather to the great velocity with which the ions move through this solvent than to the large number of ions present.

Nitric Acid.—Bouty[1] has shown that the conductivity of certain alkaline nitrates dissolved in nitric acid is very large, being of nearly the same magnitude as in water. The work is far too incomplete to enable us to draw any conclusion as to the relation between the dissociating power of nitric acid and of water. The dissociating power of the acid is, probably, very great.

Sulphur Dioxide.—That liquid sulphur dioxide has the power to dissociate salts into their ions is shown by the work of Walden,[2] on the conductivity of solutions in this solvent. He worked with seven iodides, one bromide, and two sulphocyanates, and measured their conductivities at 0°, in dilutions ranging from a few liters to 100 or 200 liters. A few of his results are given :

Potassium bromide.		Ammonium iodide.		Potassium sulphocyanate.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
14.6	30.9	20.3	36.3	10.4	17.4
29.4	30.5	30.2	37.6	22.2	17.8
38.6	31.7	54.8	43.5	36.3	19.2
50.2	33.2	91.5	49.2	53.9	20.9
71.5	35.4			73.0	22.9

Walden compared these values with those of the corresponding salts in water at 0°, and found that the conductivities in liquid sulphur dioxide are from one-fourth to one-half the conductivities in water, under the same conditions.

He determined also the molecular weights of a number of salts in liquid sulphur dioxide, by the boiling-point method, and obtained the surprising result that many of the substances which conducted, gave abnormally large molecular weights. Some results which are analogous to these were obtained by

[1] Compt. rend., 106, 595.

[2] Ber. d. chem. Ges., 32, 2862.

Franklin and Kraus[1] in liquid ammonia as the solvent. The probable explanation is that while there is some dissociation into ions, there are also molecular aggregates present of a high degree of complexity. This would account for the facts observed.

Sulphur Dichloride, Sulphuryl Chloride, Thionyl Chloride, Phosphorus Oxychloride, Arsenic Trichloride, Antimony Trichloride.—Walden[2] has quite recently studied the dissociating power of the above-named solvents, and finds that all of them break down electrolytes into their ions to a marked extent. An example or two will suffice :

Tetraethylammonium iodide in phosphorus oxychloride.		Trimethylsulphine iodide in arsenic trichloride.	
v.	μ_v.	v.	μ_v.
250	28.91	250	51.44
500	33.45	500	57.90
750	26.11	750	60.75
1500	41.60	1500	66.60

Walden also studied solutions of salts in boron trichloride, phosphorus trichloride, phosphorus tribromide, antimony pentachloride, silicon tetrachloride, stannic chloride, sulphur trioxide, and bromine, and found that these substances have little or no ionizing power. Phosphorus trichloride cannot dissociate electrolytes, while phosphorus oxychloride has a strong ionizing power; similarly, antimony pentachloride cannot dissociate electrolytes, while the trichloride dissociates to a very considerable extent. We, therefore, cannot draw any conclusion in reference to the dissociating action of a solvent, knowing the dissociation in solvents which are closely allied to it chemically.

Organic Solvents..

Methyl Alcohol.—When we turn to the organic solvents, we find that considerable work has already been done on the conductivity of electrolytes dissolved in some of them. This is especially true of methyl and ethyl alcohols. Fitzpatrick[3] studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride, and calcium chloride in methyl alcohol, and found values which, though less than

[1] This JOURNAL, **20**, 848.
[2] Ztschr. phys. Chem., **23**, 209.
[3] Phil. Mag., **24**, 378.

in water, were very considerable. Hartwig[1] measured the conductivity of formic, acetic, and butyric acids in methyl alcohol. Paschkow[2] studied the conductivities in methyl alcohol of potassium iodide, cadmium iodide, calcium nitrate, and potassium and sodium acetates. Völlmer[3] worked out the conductivities of potassium and sodium iodides, potassium and sodium acetates, and lithium chloride in methyl alcohol, for a considerable range of dilution. Holland[4] studied the effect of non-electrolytes on the conductivity in methyl alcohol of potassium, sodium, calcium, lithium, and ammonium nitrates, and sodium chloride. Carrare[5] carried out, by far, the most extensive investigation of salts in methyl alcohol which has yet been made. He measured the conductivities of the following substances at various dilutions: sodium chloride, iodide, methylate, acetate; lithium chloride, potassium chloride, bromide, iodide, methylate; ammonium chloride, bromide, iodide, and fluoride; tetraethylammonium chloride, bromide and iodide, tetramethylammonium iodide, triethylamine, diisopropylamine, and a number of sulphur derivatives. The conductivities in methyl alcohol of lithium and calcium chlorides, lithium, sodium, and barium bromides, potassium iodide, ammonium nitrate, and potassium acetate were determined by Kerler[6] in Beckmann's laboratory. The conductivity of mercuric iodide in methyl alcohol was measured by Cattaneo;[7] Schall[8] determined the conductivity of hydrochloric, picric, oxalic, and dichloracetic acids in methyl alcohol; Kablukoff[9] also studied the conductivity of hydrochloric acid in methyl alcohol; and Kahlenberg and Lincoln[10] measured the conductivities of ferric chloride and antimony trichloride in this solvent.

The most satisfactory work, on the whole, which has ever been done on the conductivity of solutions in methyl alcohol, is that of Zelinsky and Krapiwin.[11] Their work included a number of salts in pure methyl alcohol, as well as in a mixture of methyl alcohol and water, as we shall see later. They used in their work potassium bromide and iodide, ammonium bromide and iodide, cadmium iodide, tetramethylammonium

[1] Wied. Ann., **33**, 58; **43**, 838.
[2] Charkow, 1892.
[3] Wied. Ann., **52**, 328.
[4] *Ibid.*, **50**, 263.
[5] Gazz. chim. ital., **26** (1), 119.
[6] Dissertation, Erlangen, 1894.
[7] Rend. R. Acc. Linc. Roma, 1895.
[8] Ztschr. phys. Chem., **14**, 701.
[9] *Ibid.*, **4**, 429.
[10] J. Phys. Chem., **3**, 26.
[11] Ztschr. phys. Chem., **31**, 35.

bromide and iodide, tetraethylammonium iodide, a number of the substituted amines and sulphines, diethyl- and triethylstannic iodides, "fumaroid" dimethylsuccinic acid, oxalic acid, iodic acid, and trichloracetic acid.

A few of the results obtained by Zelinsky and Krapiwin are given below. These suffice to show the relation between the conductivities in methyl alcohol and in water (see p. 233).

Potassium bromide.		Ammonium iodide.		Hydroxylamine hydrochloride.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
32	69.02	16	72.24	16	54.39
64	76.70	32	78.74	32	62.18
128	83.60	64	85.0	64	69.52
256	88.96	128	91.14	128	75.98
512	93.26	256	96.20	256	81.21
1024	97.25	512	100.6	512	85.15
2048	100.1	1024	104.7	1024	87.30
4096	101.4			2048	85.70

Comparing these values of the molecular conductivity in methyl alcohol, with those of potassium chloride at the same dilution in water, we see that they are not very different. The conductivity in methyl alcohol is about two-thirds to three-fourths that in water, under the same conditions.

An examination of the above results will show that even in as strong a dissociant as methyl alcohol, it is almost impossible to reach the value of μ_∞ directly by the conductivity method. That dilution at which the salt would be completely dissociated by this solvent is so great that it is impossible to apply the conductivity method to it with any degree of accuracy. It is, therefore, not possible to measure dissociation accurately, even in methyl alcohol, by the conductivity method.

Another method has been used by Jones[1] to measure the dissociation of salts by methyl alcohol. He so improved the boiling-point method that it can be used to measure dissociation in a solvent like methyl alcohol to a fair degree of accuracy. The salts used were potassium, sodium, and ammonium bromides; potassium, sodium, and ammonium iodides; potassium and sodium acetates; and calcium nitrate. The dissociation in methyl alcohol, as found by the boiling-point method, is, in round numbers, about two-thirds of that in water under the same conditions.

Ethyl Alcohol.—The number of those who have worked on so-

[1] Ztschr. phys. Chem., 31, 114.

lutions in ethyl alcohol is quite as large as in methyl alcohol. Fitzpatrick[1] measured the conductivities of solutions of calcium chloride, calcium nitrate, lithium chloride, lithium nitrate, mercuric, magnesium, and ferric chlorides. Hartwig[2] determined the conductivity of formic, acetic, and butyric acids in alcohol. Vicentini[3] used the following chlorides: ammonium, lithium, magnesium, calcium, cadmium, zinc, and cupric, while Cattaneo[4] studied mercuric, ferrous, and ferric chlorides, cadmium bromide, and cadmium iodide. Cattaneo found that these substances have a negative temperature coefficient of conductivity. Völlmer[5] used a larger number of salts in ethyl alcohol than in water. These were potassium and sodium iodides, potassium and sodium acetates, sodium, lithium and calcium chlorides, and calcium and silver nitrates. Kawalki[6] compared the diffusion of a series of salts in water and in ethyl alcohol, and found that the rates of diffusion in the two solvents bore the same relation as the maximum molecular conductivities in these solvents. Reference should be made to the work of Paschkow,[7] who measured the conductivities in ethyl alcohol of potassium and cadmium iodides, potassium and sodium acetates, and calcium nitrate; of Schall,[8] who worked with picric, oxalic, and dichloracetic acids; of Wildermann,[9] who studied the conductivities of di- and trichloracetic acids; of Kahlenberg and Lincoln,[10] whose work in ethyl alcohol included ferric chloride and antimony trichloride; and of Kablukoff,[11] who measured the conductivity of hydrochloric acid in ethyl alcohol. The results obtained by Kahlenberg and Lincoln for the two chlorides with which they worked are given below:

Ferric chloride.		Antimony trichloride.	
v.	μ_v.	v.	μ_v.
2.89	9.91	8.11	4.18
11.57	13.70	32.45	7.94
46.28	*15.50	64.91	12.30
195.12	19.33	129.81	18.23
390.24	21.20	259.62	29.43

[1] Phil. Mag., **24**, 376.
[2] Wied. Ann., **33**, 58; **43**, 838.
[3] Biebl. Wied. Ann., **9**, 131.
[4] *Ibid.*, **18**, 219, 365.
[5] Wied. Ann., **52**, 328.
[6] *Ibid.*, **52**, 324.
[7] Dissertation, Charkow, 1892.
[8] Ztschr. phys. Chem., **14**, 701.
[9] *Ibid.*, **14**, 267.
[10] J. Phys. Chem., **3**, 26.
[11] Ztschr. phys. Chem., **4**, 429.

The dissociation of a number of salts in ethyl alcohol, as in methyl alcohol, has been measured by Jones,[1] using the boiling-point method. These include potassium and sodium iodides, sodium and ammonium bromides, potassium and sodium acetates, and calcium nitrate. These salts were found to be dissociated by ethyl alcohol to from one-third to one-fourth the extent to which they are dissociated by water, at the same dilution. It should be observed that dissociation as measured by the boiling-point method may not be directly comparable with dissociation as measured by the conductivity method, since the two sets of measurements are made at very different temperatures. It, however, seems very probable, from work which is now in progress in this laboratory, that the temperature coefficient of dissociation is quite small, in which case there should be only a small difference between the results obtained by the two methods.

Propyl and Allyl Alcohols; Isopropyl, Isobutyl, and Isoamyl Alcohols.—The dissociating power of alcohols higher in the series than ethyl alcohol has been determined for only a very few substances. A little work has, however, been done on the conductivity of a few electrolytes in the alcohols mentioned above. Schlamp[2] measured the conductivity in propyl alcohol of solutions of lithium and calcium chloride, sodium iodide, and lithium salicylate, and compared the results with those obtained in ethyl alcohol and in water. The conductivity in propyl alcohol is somewhat less than 0.5 that in ethyl alcohol, under the same conditions of concentration and temperature. Carrara[3] made a few measurements of conductivity in propyl and amyl alcohols, and Hartwig[4] determined the conductivity of formic, acetic, and butyric acids in amyl alcohol. The conductivity of triethylsulphine iodide in isopropyl alcohol was determined by Carrara.[5]

Two substances have been studied in isobutyl alcohol; hydrochloric acid by Kablukoff[6] and picric acid by Schall.[7] Their results are given below:

Hydrochloric acid in isobutyl alcohol.		Picric acid in isobutyl alcohol.	
v.	μ_v.	v.	μ_v.
0.49	2.15	101.6	1.48
2.56	3.08	307.4	1.91
50.33	3.84	511.0	2.20
136.62	3.99	638.0	2.30

[1] Ztschr. phys. Chem., **31**, 133.
[2] Ztschr. phys. Chem., **14**, 272.
[3] Gazz. chim. ital., **27**, I, 221.
[4] Wied. Ann., **33**, 48; **43**, 838.
[5] Gazz. chim. ital., **27**, I, 221.
[6] Ztschr. phys. Chem., **4**, 432.
[7] Ztschr. phys. Chem., **14**, 707.

Kablukoff[1] also worked with solutions of hydrochloric acid in isoamyl alcohol, and obtained the following results :

Hydrochloric acid in isoamyl alcohol.

v.	μ_v.
3.42	1.79
5.44	1.66
8.93	1.47
14.29	1.42
25.42	1.25

The above results bring out the remarkable fact that the molecular conductivity of hydrochloric acid in isoamyl alcohol decreases with increase in dilution. This is the first time we have encountered such a relation.

Ether.—Very little has thus far been done on the conductivity of ethereal solutions. Cattaneo[2] has measured the conductivity of ethereal solutions of cadmium iodide, cadmium bromide, ferrous and ferric chlorides, aluminium, mercurous and stannous chlorides, salicylic acid, and hydrochloric acid. The conductivities were determined at temperatures ranging from 10° to 30°, and it was found that the conductivity decreased with rise in temperature—ethereal solutions have a negative temperature coefficient of conductivity. Cattaneo also found that the molecular conductivity of hydrochloric acid in ether decreased with increase in dilution. This is analogous to the results obtained by Kablukoff, who found a similar result for hydrochloric acid in isoamyl alcohol. Indeed, Kablukoff[3] found also that the conductivity of hydrochloric acid in ether decreased with the dilution.

Acetone and Other Ketones.—The conductivities of a number of salts of the alkalies in acetone were published by Cattaneo[4] some five years ago. About the same time a paper appeared by St. v. Laszczynski[5] on the conductivity of solutions of some salts in acetone. A number of salts were included : Lithium and mercuric chlorides, potassium iodide, silver nitrate, and potassium, sodium, and ammonium sulphocyanates. The conductivity of solutions in acetone has also been measured by Carrara ;[6] but the following results are taken from the work of von Laszczynski.

[1] Ztschr. phys. Chem., **4**, 429.

[2] Atti. R. Acc. delle Scienze, Torino, **28**, 329 ; Rendic R. Acc. dei Lincei, (5), **2**, 1 sem., 295.

[3] Ztschr. phys. Chem., **4**, 431.

[4] Rend. R. Acc. dei Lincei, (5), 4°, 2° sem., 63-75.

[5] Ztschr. elek. Chem., 1895, 55.

[6] Gazz. chim. ital., **27**, I, 207.

Lithium chloride.		Potassium sulphocyanate.		Silver nitrate.	
v.	μ_v.	v.	μ_v.	v.	μ_v.
12.44	4.58	2.04	24.4	143.9	13.3
24.88	6.61	4.08	34.5	287.8	14.7
49.76	9.40	8.16	44.2	575.6	16.5
99.52	12.9	16.32	55.1		
		32.64	66.6		

Kahlenberg and Lincoln[1] measured the conductivity of solutions of ferric, cupric, and stannous chlorides, and antimony trichloride, in acetone; and Dutoit and Aston,[2] as well as Dutoit and Friderich,[3] studied a number of solutions in acetone and other ketones. Dutoit and Aston pointed out that those solvents which dissociate to the greatest extent are polymerized, as is shown by the surface-tension method of Ramsay and Shields.[4] They raise the question as to whether there is not a necessary relation between the polymerization of the solvent and its dissociating power. To test this they measured the conductivity of salts in a number of solvents. In acetone they used cadmium iodide and sodium salicylate.

In addition to acetone they worked with methylethylketone and methylpropylketone. In the former solvents they used mercuric chloride, cadmium iodide, ammonium sulphocyanate, and sodium salicylate; in the latter, cadmium iodide, ammonium sulphocyanate, and sodium salicylate. They found larger conductivity in the methylethyl- than in the methylpropylketone, but the conductivity in acetone was greater than in methylethylketone. The following data will illustrate these statements:

	Acetone. μ_v.	Methylethylketone. μ_v.	Methylpropylketone. μ_v.
CdI_2 ($v=64$)	11.6	5.58	2.13
" ($v=128$)	11.9	5.48	1.55

Dutoit and Aston conclude from their work, together with that of Kablukoff,[5] that there is a general relation between the polymerization of the molecules of a solvent and its dissociating power.

The work of Dutoit and Friderich[6] confirms that of Dutoit and Aston. They find that the values of μ_∞ for any electrolyte in different solvents, is a direct function of the amount of polymerization of the molecules of the solvent, and inversely as the coefficients of viscosity of the solvents.

[1] J. Phys. Chem., 3, 27.
[2] Compt. rend., 128, 240.
[3] Bull. soc. chim., [3], 19, 321.
[4] Ztschr. phys. Chem., 12, 433.
[5] *Ibid.*
[6] Bull. soc. chim., [3], 19, 321.

In connection with their work in acetone as the solvent they make this remarkable statement:[1] "We have found by the boiling-point method that the following salts in acetone have normal molecular weights: Cadmium iodide, lithium chloride, sodium iodide, mercuric chloride, and ammonium sulphocyanate." and these substances in acetone conduct the current. Some results already obtained in this laboratory seem to throw light on this apparent discrepancy.

Formic and Acetic Acids.—Quite an elaborate investigation on the dissociating power of formic acid was carried out by Zanninovich-Tessarin.[2] He used chiefly the freezing-point method, but also determined the conductivity of a few salts in this solvent. He measured the freezing-point lowering of formic acid produced by the following substances, at dilutions ranging from 0.34 to 3.4 normal (and in some cases at even greater concentration): Potassium, sodium, ammonium, and lithium chlorides; potassium, sodium, and ammonium bromides; hydrochloric, acetic, and trichloracetic acids. A few of his results are given:

Potassium chloride.		Sodium bromide.		Hydrochloric acid.	
Concent. normal.	Diss. Per cent.	Concent. normal.	Diss. Per cent.	Concent. normal.	Diss. Per cent.
0.341	74	1.522	51	1.82	0
1.055	62	2.509	54	2.20	0
2.263	63	4.995	60		

Formic acid is, thus, one of the strongest dissociating solvents next to water. The behavior of hydrochloric acid in this solvent is very surprising. It not only shows no dissociation in formic acid, but the molecules are actually polymerized. The conductivities of potassium and sodium chlorides in formic acid were found to be very large, and hydrochloric acid showed considerable conductivity in this solvent, although the freezing-point lowering indicated polymerization instead of dissociation. This may be due to the fact that while most of the molecules were polymerized into very large complexes, some few were dissociated into ions which carried the current.

Zanninovich-Tessarin[3] also determined the freezing-point lowering of acetic acid produced by sodium bromide and lithium chloride. The former gave normal values, indicating no dissociation, while the latter showed very marked polymerization.

The conductivity of sulphuric acid in acetic acid has been

[1] Bull. soc. chim., 334.
[2] Ztschr. phys. Chem., 19, 251.
[3] *Ibid.*, 19, 255.

measured by Jones,[1] who found that the molecular conductivity, which was small at all dilutions, increased with the dilution to a certain point ($v = 3$), and then decreased with further increase in the dilution of the solution. This is somewhat analogous to the result obtained by Kablukoff[2] for hydrochloric acid in ether and in isoamyl alcohol.

The Nitriles.—The conductivities of mercuric chloride, sodium bromide, cadmium bromide and iodide, ammonium sulphocyanate and silver nitrate, in propionitrile, were determined by Dutoit and Aston.[3] This investigation was extended by Dutoit and Friderich[4] to solutions in acetonitrile and butyronitrile. The dissociating power of these three related substances can be seen from the following figures:

Silver nitrate.	Acetonitrile.	Propionitrile.	Butyronitrile.
	μ_v.	μ_v.	μ_v.
$v = 8$	54.5	14.21	....
$v = 128$	118.3	34.42	23.8
$v = 256$	131.5	38.86	35.5

The dissociating power is obviously greater in the first members of the series of nitriles, and becomes less as we ascend the series.

Pyridine.—Our knowledge of the dissociating power of pyridine we owe almost entirely to St. v. Laszczynski and St. v. Gorski.[5] They measured the conductivities of lithium chloride, potassium, sodium, and ammonium iodides, and potassium, sodium, and ammonium sulphocyanates in pyridine, over a wide range of dilutions. A few of their results are given:

Potassium iodide.		Sodium sulphocyanate.	
v.	μ_v.	v.	μ_v.
178.49	22.04	32.24	7.98
713.9	30.68	128.96	12.79
2855.6	38.05	515.84	20.56

The conductivities are very considerable in this solvent.

Werner[6] found that certain inorganic salts in pyridine conduct very well, and yet show little or no dissociation by the boiling-point method.

[1] This JOURNAL, **16**, 13.
[2] *Loc. cit.*
[3] Compt. rend., **128**, 240.
[4] Bull. soc. chim., (3), **19**, 321.
[5] Ztschr. elek. Chem., **4**, 290.
[6] Ztschr. anorg. Chem., **15**, 1, 39.

Other Organic Solvents.—A few measurements of the conductivity of one or more substances in a number of solvents have been made, but the work with any one of the remaining solvents is so slight that it does not call for special treatment. Thus, Werner[1] found that cuprous chloride in ethyl sulphide conducts very poorly. Cattaneo[2] studied a few solutions in glycerine and found that they had larger conductivity than the corresponding solutions in ether. They also had larger temperature coefficients of conductivity. Kablukoff[3] measured the conductivity of hydrochloric acid in benzene, xylene, and hexane, and showed that solutions in the hydrocarbons conduct very poorly.

Dutoit and Aston[4] measured the conductivity of electrolytes in benzene chloride, ethyl iodide, ethyl bromide, and amyl acetate, and found that solutions in these solvents conducted very poorly. They found, on the other hand, that solutions in nitroethane conduct very well. Dutoit and Friderich[5] worked with acetophenone as solvent, and with cadmium iodide, mercuric chloride, and ammonium sulphocyanate as electrolytes. The conductivity in this solvent was small.

Four other solvents have thus far been studied—ethyl acetate, ethyl acetoacetate, benzaldehyde, and nitrobenzene. This work has been done by Kahlenberg and Lincoln.[6] As electrolytes they used ferric and stannous chlorides, bismuth trichloride, and antimony trichloride. The conductivities in these solvents are, in general, small, but vary considerably with the nature of the electrolytes used.

Mixed Solvents.

Hydrogen Dioxide and Water.—The dissociating power of a mixture of hydrogen dioxide and water has not yet been measured, but Calvert[7] has found that the dielectric constant of such mixtures is greater than that of pure water. He employed the beautiful method of Drude, and from the dielectric constant of the mixture he calculated the dielectric constant of pure hydrogen dioxide to be 92.8 at 18°. The dielectric constant of pure water at this temperature is, according to Drude, 81.

J. J. Thomson[8] pointed out, as has already been mentioned,

[1] Ztschr. anorg. Chem., **15**, 1, 39.
[2] Beibl. Wied. Ann., **17**, 365.
[3] Ztschr. phys. Chem., **4**, 429.
[4] Compt. rend., **125**, 240.
[5] Bull. soc. chim., [3], **19**, 325.
[6] J. Phys. Chem., **3**, 12.
[7] Ann. der Phys., **1**, 483.
[8] *Loc. cit.*

that there is probably a very close relation between the dielectric constants of solvents and their dissociating power. We shall see that while the two are not proportional, there is undoubtedly a qualitative relation between them. It is, therefore, very probable that the dissociating power of hydrogen dioxide is greater than that of water. This would not be very surprising, since many of the properties of hydrogen dioxide are simply the properties of water intensified. Work on this problem is now in progress in this laboratory.

Mixtures of Water and the Alcohols.—A number of experimenters have worked with mixtures of water and one or another of the alcohols. We should mention the work of Lenz,[1] Stephan,[2] Kerler,[3] Kablukoff,[4] Carrara,[5] Schall,[6] and Arrhenius.[7] Quite an elaborate investigation on the conductivity of electrolytes in mixtures of water and ethyl alcohol, was carried out by Wakeman.[8] His work had to do chiefly with the organic acids in mixtures of these solvents containing varying amounts of alcohol. The results showed that the conductivity became gradually smaller as the amount of alcohol present became larger and larger—just as would be expected from the relative conductivities in these two solvents.

But results of a very different character were obtained by Zelinsky and Krapiwin[9] in mixtures of methyl alcohol and water. It will be remembered that electrolytes in methyl alcohol conduct, in general, to a much smaller degree than in water; yet certain salts were found to have greater conductivity in pure methyl alcohol than in a mixture of 50 per cent methyl alcohol and 50 per cent water. This is shown by the following table, taken from the work[10] of Zelinsky and Krapiwin:

[1] Mem. de l'Acad. de St. Petersbourg, (7), 30, 1881.
[2] Wied. Ann., 17, 673.
[3] Dissertation (Erlangen), 1884.
[4] Ztschr. phys. Chem., 4, 432.
[5] Gazz. chim. ital., 16, 1.
[6] Ztschr. phys. Chem., 14, 701.
[7] *Ibid.*, 9, 487.
[8] *Ibid.*, 11, 49.
[9] *Ibid.*, 21, 35.
[10] *Ibid.*, 21, 49.

Potassium Bromide.

	Water.	Methyl alcohol.	Methyl alcohol, one-half; water, one-half.
v.	μ_v.	μ_v.	μ_v.
16	123.1	....	59.82
32	127.5	69.02	62.46
64	130.5	76.70	65.36
128	132.9	83.60	67.11
256	136.4	88.96	69.26
512	140.2	93.26	70.53
1024	143.4	97.25	....

Ammonium Iodide.

16	125.4	72.24	62.63
32	129.6	78.74	65.04
64	133.4	85.0	67.48
128	135.9	91.14	69.28
256	138.7	96.20	70.34
512	141.3	100.6	71.12
1024	143.7	104.7	71.57

It is impossible at present to say what these surprising and very remarkable results mean. They are confirmed by the work of Kerler and of Carrara.

Similar results were obtained by Cohen[1] with ethyl alcohol and water, but only when the mixture contained very little water and at dilutions which were quite large, as is shown by the following table:

Potassium Iodide.

	Pure alcohol.	80 parts alcohol and 20 parts water.
v.	μ_v.	μ_v.
64	26.1	30.9
128	29.2	32.2
256	31.8	33.2
512	34.4	34.1
1024	36.0	34.5
2048	36.3	35.0

The conductivity in the mixture is the greater, until a dilution of 512 liters is reached, when the conductivity in the pure alcohol becomes greater than in the alcohol containing 20 per cent of water.

Cohen found, however, for most substances that the presence of water in the alcohol increased the molecular conductivity, as we would expect.

[1] Ztschr. phys. Chem., **25**, 31.

Conclusions from the Work thus far Done.

An examination of the work described in this review will show that different solvents have very different ionizing power. With the possible exception of hydrogen dioxide water is the strongest ionizer. Next to this comes formic acid. Of the more common solvents, methyl alcohol dissociates to a much greater degree than ethyl alcohol. Indeed, it is true, in general, that *in an homologous series of solvents the lower members have the greater dissociating power.*

It has already been mentioned that attempts have been made to discover relations between the ionizing power and other properties of a solvent. Thomson's theory that the dissociating power and the dielectric constants of solvents should stand in very close relation to each other, undoubtedly contains a large element of truth. Those solvents which have the largest dissociating power, have, in general, the largest dielectric constants. A number of independent investigations have shown that these two properties are not proportional.

The suggestion of Dutoit and Aston that there is a connection between the amount of association of the molecules of a solvent, and its power to ionize electrolytes, undoubtedly contains much truth. Thus, the molecules of water are associated to a greater extent than those of any other liquid, as Ramsay and Shields have shown. The molecule of liquid water at ordinary temperatures is $(H_2O)_4$. Similarly, the alcohols and other strongly dissociating solvents show considerable association of their molecules.

It will probably be shown that the dissociating power of a solvent is not a function of any one physical or chemical property of the substance, but of them all. Or, perhaps, more accurately expressed, all the properties of a substance are a function of the energy relations which obtain in that substance, and ionizing power is simply one of these properties.

The conclusion from this work which is of chief importance for pure chemistry is that ions are almost always present when chemical reaction takes place. When the number of solvents which can effect ionization to some extent is considered, and the fact that heat and possibly pressure can dissociate molecules, it will be seen that there is scarcely a chemical reaction in which ions, as well as molecules, are not present. The question then arises: Which causes the reaction, the ions or the molecules? This can be answered by excluding ions and then observing whether chemical reaction takes place or not. This has been done with the following results: Hydrochloric acid gas dried and dissolved in dry chloroform does not conduct the current and is, therefore, not dissociated. Under

such conditions it will not decompose carbonates. Liquid hydrochloric and sulphuric acids when free from water will not turn litmus red. Dry hydrochloric acid gas and dry ammonia gas do not react to the slightest extent. Still more surprising, perhaps, is the fact that sulphuric acid free from water will not react upon dry metallic sodium. Special precautions must be taken, of course, in all such cases to remove every trace of moisture.

The above examples might be largely increased, but these suffice to show the chemical inertness of molecules. We are now in a position to say that most chemical reactions, if not all, are reactions between ions, and molecules as such do not enter into the reactions at all. As the reactions proceed and the ions already present are used up, the molecules are gradually dissociated and furnish new ions which then enter into the reaction. The chemistry of atoms and molecules has thus given place to the chemistry of ions.

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January 1, 1901.

REVIEWS.

A MANUAL OF ASSAYING: The Fire Assay of Gold, Silver and Lead, Including Amalgamation and Chlorination Tests. By ALFRED STANLEY MILLER, Professor of Mining and Metallurgy, University of Idaho. First Edition. New York: John Wiley and Sons. 91 pp. $1.00.

The author's preface says "The plan of this book is a departure from the books on this subject with which the writer is familiar. The apparatus is brought in where its use is easily understood. The student is taught the operations of the fire assay by practising with an ore easy to assay. He is then better prepared to understand the directions for assaying more complex ores."

The author has succeeded admirably; he notes and explains all the details which confuse a beginner, and the student is led onward step by step.

This little work may be recommended as a college manual; it contains enough for the college student, and covers its limited subject fully.

E. R.

A TEXT-BOOK OF IMPORTANT MINERALS AND ROCKS, with Tables for the Determination of Minerals. By S. E. TILLMAN, Professor of Chemistry, Mineralogy, and Geology, U. S. Military Academy, West Point, N. Y. First Edition. New York: John Wiley and Sons. 186 pp. $2.00.

This book comprises a brief descriptive chapter on the elements of crystallography, another on the physical and chemical properties of minerals, another devoted to descriptive

mineralogy, a set of tables for the determination of minerals, and a brief chapter on common rocks. It is, in short, a condensed manual of determinative mineralogy adapted to the needs of an institution where a book like that of Brush and Penfield would be too large. E. R.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY, AND BLOWPIPE ANALYSIS FROM A PRACTICAL STANDPOINT. By ALFRED T. MOSES AND CHARLES LATHROP PARSONS. Enlarged new edition. New York: D. Van Nostrand Company. 1900. 8vo. vii + 414. 664 figs. $2.00 net.

The publication of a second edition of this text-book shows that the clear, concise statements of the essential facts regarding the mineralogical distribution of the principal chemical elements have been well received. In the new, revised, and enlarged edition the crystallography of minerals, according to the chapter on crystallography, has been rewritten to conform to the modern classification of crystals in 32 classes. The presentation is clear and sufficiently full for ordinary courses in colleges and mining schools. Unlike the first edition, the second gives a summary of the optical, thermal, magnetic and electrical characteristics of the different crystal systems.

The second part, dealing with blowpipe analysis, has been revised and somewhat amplified by additions concerning the use of the spectroscope and metallic sodium.

The descriptive mineralogy, forming Part III, presents the minerals grouped according to their most important economic element. The composition, physical features and behavior before the blowpipe are succinctly given and short statements are made regarding the uses of each mineral and the various species with which it may be confused. The selection of minerals for treatment in this part of the volume is, on the whole, in excellent proportion. The differences in economic importance are emphasized by the use of different types. The determinative mineralogy has been entirely rewritten and greatly simplified and the tables have been improved by breaking them up into several smaller groups.

The illustrations of the second edition are a great improvement over the former issue, but the retention of a few cuts of the former style of drawing detracts somewhat from the general tone of the work. E. B. M.

LEHRBUCH DER ANORGANISCHEN CHEMIE (Second Edition). By DR. HUGO ERDMANN, Professor at Halle. Braunschweig: Vieweg und Sohn. 1900. xxvi + 758 pp.

The first edition of this book has already been reviewed in this JOURNAL.[1] The fact that a new edition has appeared in

[1] This JOURNAL, **30**, 874 (1898).

so short a time is evidence that the virtues of the book have made a greater impression than its faults. The second edition contains reference to many new facts which have been discovered since the earlier printing, and gives a somewhat fuller historical treatment in some cases; but, nevertheless, it is essentially unchanged in plan and substance. A careful comparison of the very detailed tables of contents shows the only important alteration in arrangement to have been the questionable shifting of tellurium from its companionship with selenium. It is now to be found among the noble metals, in association with osmium and ruthenium. This adherence to the letter of the periodic table leads one to expect to find more prominence given to this table, even if its spirit is disregarded; but the table is still only to be found in the midst of the singularly cramped confusion of the final chapter.

Many of the earlier misprints have been corrected, and only occasionally does one meet with such a new one as the ascription of "Aetherion" to "Brugh." Among the new facts recorded, the chapter on the noble gases is especially interesting and important, not so much on account of the brilliant chromolithographs of their spectra, as because Professor Ramsay is said to have read the proof.

As before, the weakest side of the book is the lack of unity and clearness in its theoretical framework. Many examples of this deficiency might be cited. For instance, the idea that nitric acid somewhat diluted with water undoubtedly has the formula $N(OH)_5$ is still advanced. The word "phase" does not occur in the index, and does not seem to have been mentioned. Neither does any general reference to the effect of concentration on the direction and progress of a chemical reaction seem to have found a place in the book.

An example of the difference between a veiled and uncomprehending statement and a logical illuminative explanation may be seen on comparing the treatment of the cause of oven-burning plaster of Paris, on p. 529, with that given by Ostwald on p. 531 of the new "Grundlinien"; or on comparing the statements concerning the changing solubility of sodic sulphate, on p. 508, with that given in any modern work on physical chemistry. One cannot but regret that the unusual wealth of material contained in this book should have received so little illumination from modern theory. T. W. R.

QUANTITATIVE CHEMICAL ANALYSIS, Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc. (London), and J. BERNARD COLEMAN, A.R.C.Sc. (Dublin). Fifth Edition. Philadelphia: P. Blakiston's Son and Co. 1900. xxiv + 592 pp. Price, $3.50.

This book is offered as a text-book for students, teachers,

and others, and is a compendium of general quantitative analysis. The subject-matter has been arranged in seven principal parts, which are subdivided into sixteen sections.

Part I. deals with the preliminary and general operations, such as weighing, determination of specific gravity, preparation of pure substances, and of substances for analysis; Part II. is devoted to simple gravimetric estimations; Part III. treats of volumetric analysis, standard solutions, and calibration of apparatus; Part IV. contains descriptions of more complex gravimetric and volumetric determinations. This section of 217 pages includes the analysis of ores, industrial products, water, food, and organic substances; Part V. treats of gas analysis; Part VI. contains typical results of analyses, tables of constants, specific gravities, and atomic weights; Part VII. gives descriptions of the preparation of gases, use of compressed gases, and the distillation of water. An appendix contains a chapter on some new forms of apparatus, and some recent analytical methods.

By omitting all theoretical considerations, and with the frequent use of cross references, the authors have condensed into 592 pages almost the whole subject of quantitative analysis, and for the most part successfully. When so much material, however, is crowded into such a small space, some of it is sure to suffer. This is particularly true of the more special subjects included in Part IV. The most accurate and most approved methods for the determination of carbon, manganese, and phosphorus in steel are not given. The excellent method of Gibbs for the precipitation of manganese as manganese ammonium phosphate, and the volumetric methods for manganese and phosphorus are not mentioned. The convenient volumetric methods for the determination of fat in milk such as those of Babcock, and Leffmann and Beam are omitted. The subject of electrolytic separations is almost entirely neglected. This is especially so on page 282 where an excellent opportunity presents itself for the electrolytic estimation of copper, lead, and tin in an alloy of those metals.

It is much to be regretted that no references to original articles are given. In the appendix is given a list of text-books for reference, but it would have been much more profitable and useful to have given the authority for many of the processes. It is easy, however, to find fault, and it is not the intention of the reviewer to leave the subject without saying that there is much in the book which is excellent. H. F.